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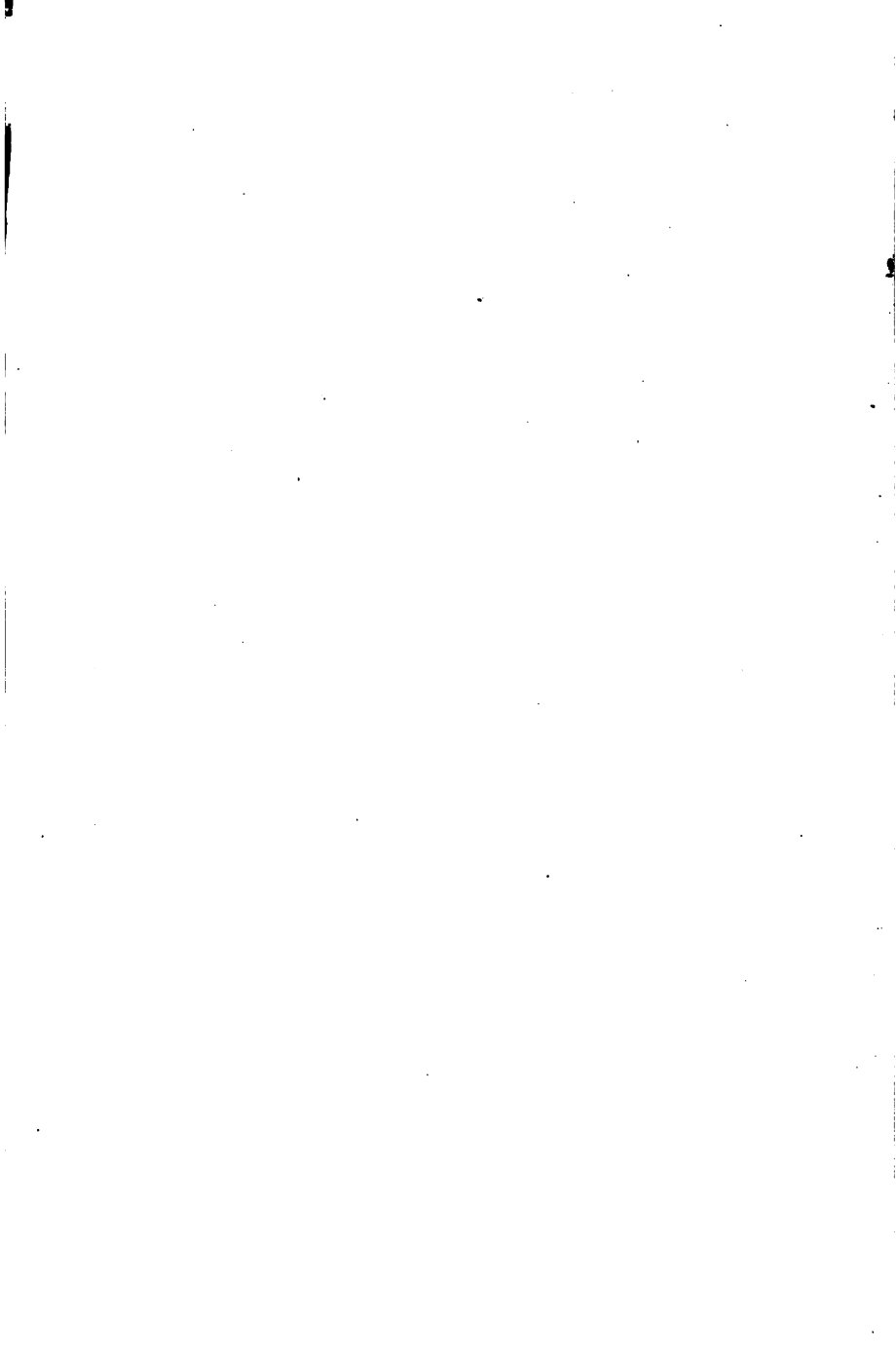
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# **Corrosion of Iron and Steel**

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# The Corrosion of Iron and Steel

By

Alfred Sang

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## PREFACE

The corrosion of iron and steel is one of the leading questions of the day among engineers, metallurgists and manufacturers. Information on the subject is widely scattered and its value is thereby greatly reduced.

This essay is based on a paper read before the Engineers' Society of Western Pennsylvania, at Pittsburgh, December 15, 1908, and published in the Proceedings.

The work is in great measure a compilation and study of the results obtained by other investigators and is intended as a compendium of the subject suitable for reference.

I am indebted to Mr. Harrison W. Craver for the free use of the extremely valuable bibliography of the subject published by the Carnegie Library of Pittsburgh, which is reproduced in condensed form at the end of the volume.

ALFRED SANG

96 Boulevard de Versailles

Saint Cloud (S. & O.), France

September 6th, 1909



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# **Corrosion of Iron and Steel**

## 2 THE CORROSION OF IRON AND STEEL

roof of a gas-works in New York City which collapsed for lack of attention, forecasted a similar fate sooner or later for structures like the viaducts of the elevated railway of the same city, which almost casual observation will show are repainted over the rust without any preliminary cleaning.

On account of this necessity of combating corrosion, it is imperative that engineers arrange the design so that every part of structural works be readily accessible for frequent inspection. It has been truly said that "wrought iron is not only a bad but a dangerous material if neglected"; this is far more true of steel, because, starting from a higher tensile strength, it decays as rapidly, and often more rapidly, than iron, down to the point of failure.

## COMPOSITION OF RUST

In order to bring about improvements in the protection of metals from corrosion, it is necessary to study the nature of this corrosion; to devise either preventives or cures the disease itself must be understood.

Rust is a ferric sesquioxide ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ) which may or may not be hydrated; it is of a brown, red-brown or yellow-brown color; when formed under water it is generally of a deeper tint and is of a somewhat colloidal nature. Rust formed by the rapid evaporation of water on the surface of iron is usually of a deep red-brown color, has a shiny appearance and is high in combined water. Oxidation at a high temperature yields the magnetic oxide,  $\text{Fe}_3\text{O}_4$ .

The composition of rust varies within narrow limits; magnetic oxide ( $\text{Fe}_3\text{O}_4$ ) is always present (Tilden); according to Toch, the rust nearest the iron is highly ferrous, blending outwardly into a more stable oxide; this is due to the progressive way in which the decomposition takes place; Andrews has shown that the rate of decomposition also increases progressively, being, under the conditions of his experiments, about 50 per cent more

#### 4 THE CORROSION OF IRON AND STEEL

rapid the second year than the first. Rust also contains some ferrous carbonate.

Moody gives<sup>1</sup> the following data on the rust from the inside of some iron tanks which had been in constant use:

	No. 1.	2.	3.	4.	5.	6.
% Iron as ferric oxide.....	55.73	51.12	64.60	65.13	68.89	67.46
% Iron as ferrous oxide.....	32.86	36.57	25.74	25.66	23.18	24.40
% Iron as ferrous carbonate..	11.40	12.31	9.66	9.21	7.93	8.14

Rust from lot No. 1 was crushed and exposed to the air during eight days, resulting in a great increase of the more stable ferric oxide ( $\text{Fe}_2\text{O}_3$ ), the ferrous oxide ( $\text{FeO}$ ) falling to 14.11% and the ferrous carbonate ( $\text{FeCO}_3$ ) to 5.62%.

Recent analyses\* of rusts formed by the total decomposition in the open air under normal conditions of a mild steel rivet rod, a light steel rail, a steel sheet as used for roofing and an iron chain link, gave the following results, the  $\text{FeO}$  and  $\text{CO}_2$  being corrected to magnetic oxide and carbonate, respectively:

	Rod.	Rail.	Sheet.	Chain.
Free Moisture.....	.12	.11	.24	.08%
Ferric Oxide ( $\text{Fe}_2\text{O}_3$ ).....	85.41	84.92	80.96	80.55
Magnetic Oxide ( $\text{Fe}_3\text{O}_4$ ).....	.541	1.77	4.41	20.66
Ferrous Carbonate ( $\text{FeCO}_3$ ).....	.84	2.24	.95	.81
Manganese Dioxide ( $\text{MnO}_2$ ).....	.41	.73	.54	.06
Carbon & carbonaceous matter....	.15	.93	1.17	.20
Combined water.....	5.90	6.60	9.42	3.88
Silica and Insoluble matter.....	.14	.05	1.50	1.44
Undetermined .....	1.74	2.76	1.05	2.94

It will be noticed that in all cases the amount of magnetic oxide is in inverse ratio to the manganese content. The magnetic oxide in the rail and sheet rusts is evidently due to the original mill-scale, but in the rod, which had remained exposed during over

\* Made for the author by Mr. J. J. Miller.

four years, it is much higher; the very high percentage in the chain which had been corroding during 15 years or more in the mud of the Panama Canal zone\* may bear some relation to the fact that after being brought into the air in an apparently sound condition it rapidly disintegrated, probably owing to the rapid oxidation of unstable ferrous oxide ( $\text{FeO}$ ) or its combination with  $\text{Fe}_2\text{O}_3$  to form  $\text{Fe}_3\text{O}_4$ .

Rust is not crystalline; it is granular and amorphous; very ancient rust is, however, said to consist of a mixture of magnetic oxide and anhydrous sesquioxide in a more or less crystallized condition, not unlike the crystalline hematite, or oligistic iron, abundant in Elba, but also found in other iron-ore regions. The higher proportion of  $\text{Fe}_3\text{O}_4$  and low proportion of combined water in the chain rust from Panama would appear to confirm this. It is also claimed that ammonia may be formed during rusting, as in the case of organic matter undergoing decomposition; Bloxam and others claim that ammonia is formed from the nitrogen of the air during the process of rusting.

---

\* This chain link was supplied by Mr. A. E. Crockett, Gen. Mgr. of the Standard Chain Co.

## FORMATION OF RUST

Under ordinary conditions, corrosion never seems to take place evenly; upon closer investigation it is found that it does not and cannot take place evenly; this is due to "pitting." The rust commences to form at distinct points which must therefore be particularly liable to attack; the spreading of the rust from these original points is like that of a disease. There is a peculiar formation known as "tubercular corrosion" which owes its name to the wart-like concretions of rust and earthy matter derived from the water, which grow on the metal; this form of corrosion is specially frequent in cases where alkalies and saline matter are present together in a highly aerated water; it is common in water-mains. If the "tubercle" is removed, a hole is found in its place.

Rusting starts at certain points and spreads out until the different growths unite into a continuous covering. The theory of pitting, due to John, is that at the point where it takes place there is a speck of impurity, such as a particle of slag or scale, or a segregated constituent of the metal, which gives rise to galvanic action.

Where pitting is serious, corrosion may reach through a plate long before the greater part of the surrounding surface is seriously rusted. Were corrosion to take place evenly, the life of the material would be greatly extended. In proof of this Mallet made a series of experiments<sup>2</sup>; they were carried out on large surfaces and at ordinary temperatures over a long period of time; he found the following *average relative* depths of corrosion, corrected for one century of time, for steel and wrought iron taken together:

In the atmosphere and freely exposed to the weather .....	0.0343	of an inch
In fresh river water.....	0.0352	" " "
In clear open sea-water.....	0.3263	" " "
In sewage-fouled sea-water.....	0.5327	" " "

The tables of actual results with various grades of iron and steel which yielded the above averages are very instructive, although the chemical compositions and physical conditions must in many, if not all, cases have differed from those of equivalent qualities manufactured nowadays.

As seasons and conditions recur, rust forms in layers which can be detached from each other. Being more or less spongy and perhaps hygroscopic, it will retain moisture in close proximity to the iron, besides giving rise to an unfavorable voltaic action. Prof. W. H. Gee states<sup>3</sup> that a bright steel in contact with the same steel after rusting 24 hours in the atmosphere of Manchester, showed a difference of potential of 0.104 v. Rust in contact with iron hastens its corrosion by acting, therefore, as a depolarizer; it is very voluminous and

## 8 THE CORROSION OF IRON AND STEEL

may occupy as much as ten times the space of the original iron (Ward and Bauerman). It may also act as a carrier for oxygen, furnishing it to the iron and replacing it from the air. These properties promote the growth of rust both laterally and in depth.

Rusting is the reverse of the process of iron smelting; the corrosion of iron to the sesquioxide must release the same number of calories as would be absorbed in converting a natural sesquioxide into iron.

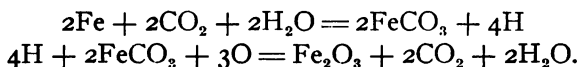
As will be seen presently, while there is considerable doubt as to the necessity of an acid being present to cause rusting, there is no doubt whatever about the necessity that both oxygen and water be present; it is generally agreed that the moisture must be able to condense on the surface of the metal. This is by no means proven, although theoretical considerations require that the water be in the liquid form.

There are three theories of rusting, and in examining them it is well to bear in mind that, while one or other of them may explain the true first cause of rusting, the others may, and some of them undoubtedly do, present conditions which, if not essential, at least intensify the decomposition. A summary of theories has been published by Mugdan.<sup>4</sup>

### CARBONIC ACID THEORY

The oldest of the plausible theories of corrosion, whose chief supporters have been Dr. F. Crace Calvert<sup>5</sup> and Prof. Gerald T. Moody,<sup>6</sup> supposes that carbonic acid attacks the iron, converting it into a carbonate and releasing hydrogen, which unites with the oxygen present, as air or otherwise, to decompose the ferrous carbonate to ferric hydroxide, or rust, leaving the same amount of acid as was originally present to react as before and form more rust.

The nature of the reaction may be described as follows:



The carbonic acid may be written  $\text{H}_2\text{CO}_3$  and the residual  $2\text{H}_2\text{O}$  may be applied to the hydration of  $\text{Fe}_2\text{O}_3$  and  $\text{CO}_2$ .

The theory is a logical one. The objection that it is not proved that iron will not rust in thoroughly boiled distilled water is not insuperable. Stéphane Leduc has shown that it is impossible to extract all of the dissolved gases from distilled water by boiling; he claims that not less than one cubic centimeter of gas would be left in one liter of

## 10 THE CORROSION OF IRON AND STEEL

water, which it is impossible to remove. Part of this gas must, almost certainly, be carbonic dioxide, of which there is 0.04 per cent present in the atmosphere; it is more soluble in water than the oxygen and nitrogen of the air.

The operation of rusting being, according to this theory, a cyclical or regenerative one, it has been argued (Whitney) that a single molecule of carbonic dioxide would be sufficient to start and maintain corrosion in the presence of air and water. The carbonic acid, due to the reaction of the carbonic dioxide with water, would help iron into solution; this is all that is necessary to corrosion, the dissociated iron or, more likely, the ferrous carbonate being oxidized to rust in the presence of oxygen. If, however, this residual gas in water cannot be removed by physical means, such as boiling, it might be feasible to do so chemically; this may be the case with oxidizing agents used as rust inhibitors, to be referred to later; even then it is possible that a definite degree of concentration of the acid neutralizer would have to exist, as the rusting of iron in weak alkaline solutions would seem to indicate.

Prof. A. Crum Brown has described, as follows, the rusting of iron by a drop of water in the presence of  $\text{CO}_2$ :<sup>7</sup> "At first, for a short time, the drop remains clear, and the bright surface of the iron is seen through it; but soon a greenish precipitate forms in the drop, and this rapidly becomes reddish brown. This brown precipitate does not

adhere to the iron, but is suspended in the water and becomes a loosely adherent coating only when the water has evaporated."

The careful investigations of Dr. A. S. Cushman<sup>8</sup> and others seem to show, almost conclusively, that rusting will take place when there is no carbonic acid present; when there is, a greenish carbonate is formed, which promptly changes to the hydroxide when oxygen is supplied to it. While the carbonic acid theory may accurately describe how rusting does actually take place under normal conditions, and be, therefore, correct, there seems to be little reason to doubt but that rusting can take place without its aid. This conclusion, based on the valuable work of Cushman and Walker, agrees with what Mallet wrote in 1872: "If the air contains vapour of water, however, chemical action rapidly occurs, more rapidly if carbonic acid also be present. The presence of the latter is, however, not necessary to initiate the action, as has been stated by Calvert."

Carbonic acid will greatly increase the rate of corrosion. The following figures, giving the loss in milligrams per square inch of surface for two grades of iron of exceptional purity and two steels of ordinary quality, are typical:<sup>9</sup>

5 Hrs. in	Aerated Water.	Aerated Water and CO <sub>2</sub>	Increased loss due to CO <sub>2</sub> .
Iron No. 1.....	2.70	4.45	66%
Iron No. 2.....	2.60	4.42	70%
O. H. Steel.....	3.17	5.25	66%
Steel Nipple .....	3.76	5.32	42%

Prof. Moody to show the importance of the action of CO<sub>2</sub> gives the following figures<sup>10</sup> showing

## 12 THE CORROSION OF IRON AND STEEL

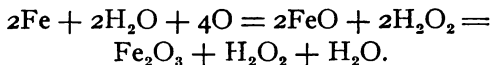
the percentage of the total oxygen in 100 c.c. of air which were taken up by 10 grams of iron:

		Ord. Air and dist. water.	Air and water; almost entirely freed from CO <sub>2</sub> .
After	6 Hrs.....	5.7	None
"	24 ".....	29.1	None
"	72 ".....	61.3	0.9
"	168 ".....	94.3	3.8

The conclusions of E. Heyn and O. Bauer concerning the effect of CO<sub>2</sub> in rusting, derived from their recent researches,<sup>11</sup> are as follows: 1. Iron will rust under conditions in which CO<sub>2</sub> is absolutely absent. 2. Air containing 15% of CO<sub>2</sub> under the same conditions is only twice as active as air absolutely free from CO<sub>2</sub>. It is not likely or possible that the small amount present in the atmosphere exerts any action on the process of rusting. 3. Pure CO<sub>2</sub> causes no peculiar rusting. It acts as any acid by dissolving with the evolution of hydrogen.

### HYDROGEN PEROXIDE THEORY.

The second theory of rusting, originally due to Traube,<sup>12</sup> is known as the peroxide theory. According to this theory, the iron, oxygen and water are supposed to react to form ferrous oxide (FeO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which then unite to form the ferric hydroxide, leaving an excess of hydrogen peroxide which attacks a new quantity of iron. The reaction might be somewhat as follows:



While it is true that iron immersed in commercial peroxide shows a red precipitate of rust, it has been found impossible to detect the presence of hydrogen peroxide during ordinary rusting, and while this failure may not condemn the theory, it makes it appear improbable. Both Moody and Cushman claim that iron does not rust in pure neutral hydrogen peroxide.

## ELECTROLYTIC THEORY

The third and most widely accepted theory is the electrolytic one.

When two substances of different polarity are immersed in a suitable electrolyte—or medium containing free ions of matter—an electric current is set up, and the substance from which the current flows tends to dissolve. Whether or not this “galvanic solubility” explains all solubilities, or, as generally believed, *pure* metals have a solution tension similar to the diffusion of *gases*, is a matter for investigation. So far as corrosion is concerned, the electrolytic theory implies the solution of the iron in water or moisture as ferrous ions; the iron, while in this dissociated condition, is oxidized by any free oxygen present. To quote Dr. Cushman:<sup>13</sup> “If, therefore, we immerse a strip of iron in a solution containing hydrogen ions iron will go into solution, and hydrogen will pass from the electrically charged or ionic to the atomic or gaseous condition. In such a system the solution of the iron and, therefore, its subsequent oxidation, must be accompanied by a ‘precipitation,’ or setting free of hydrogen. It is very well known that solutions of ferrous salts as well as freshly precipitated ferrous hydroxide are

rapidly oxidized by the free oxygen of the air to the ferric condition, so that if the electrolytic theory can account for the original solution of the iron the explanation of rusting becomes an exceedingly simple one."

Thus, Dr. Cushman explains—and in this he is in agreement with Dr. Walker—that hydrogen ions must be present, either from dissociation of the water or otherwise, before solution can take place. The natural tendency of the metal to dissolve puts ions of iron into solution, and, in order to restore electrostatic equilibrium, the hydrogen is precipitated in a gaseous condition. It is extremely doubtful as to there being any hydrogen actually precipitated in ordinary corrosion; there would usually be sufficient dissolved oxygen present to oxidize the nascent hydrogen. It is commonly taken for granted that there is always a certain degree of dissociation in water, but this remains as yet unproven; in ordinary water it may well be the case on account of the presence of impurities.

The process of rusting, stated in Dr. Walker's words, is as follows:<sup>14</sup> "When a metal is placed in water or in an atmosphere sufficiently moist so that a film of water condenses on its surface, the action which may take place is essentially one of solution. Every metal has a tendency to pass into water solution in the ionic form, assuming a positive charge of electricity and leaving the metal negatively charged. To maintain electrostatic equilibrium, an equivalent amount of positive electricity

must leave the solution by the separation of hydrogen ions from the dissociated water in the form of hydrogen gas, charging that portion of the metal on which the hydrogen separates positively, and leaving the solution negatively charged. An electrolytic current is thus produced which is carried from one point on the iron to the solution by the escaping iron ions, and from the solution again to the iron by the separating hydrogen ions, and equilibrium again restored. The speed of this reaction depends, *first*, upon the escaping tendency of the metal itself, measured by its solution pressure; *second*, upon the concentration of the hydrogen ions, increasing as this concentration is increased; *third*, upon the ease with which deposited hydrogen ions can assume a gaseous state and escape or be removed from the metallic surface."

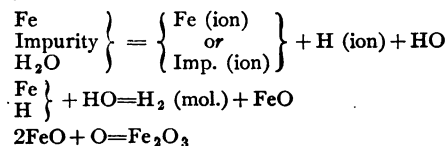
The second and third points relating to hydrogen will receive further attention in a subsequent section. As regards the assumption that "every metal has a tendency to pass into water solution in the ionic form," it is worth pointing to the well-established fact that solution-tension varies more or less as the polarity; metals which are negative to hydrogen, all conditions being equal, are endowed with less "solution pressure" than those which are positive to it. It is justifiable to claim relationship between these two properties.

It is erroneous to say that iron only corrodes when anode. Ordinary iron corrodes, whatever the galvanic position of the mass may be in reference

to its surroundings; as will appear later, all that is necessary besides the electrolyte to cause corrosion is a few voltaic couples in the mass, or else, as just stated, free dissociated hydrogen in contact. Iron as cathode is less liable to corrosion, and this fact is taken advantage of in engineering work, to inhibit rusting.

The electrical inoxidation process of de Meritens<sup>15</sup> seems to be a reproduction on a rapid scale of the process of electrolytic corrosion. Iron containing occluded, and therefore presumably dissociated, hydrogen, and immersed in warm distilled water, is rusted by connecting it to the positive pole of a battery supplying a current of low voltage; if the current is as weak as can be made to pass through the water, the formation is one of black oxide, or the rust is converted into black oxide. If the iron is free from hydrogen it is necessary to first connect it to the negative pole so that it may absorb some, else the action will not take place. The part played by hydrogen in this process is most interesting and bears out the statement of Dr. Cushman which has been quoted, giving it, however, more exact significance; it would seem that the hydrogen ions may be dispensed with in the solution if they are occluded in the iron. Hydrogen is not merely a by-product in the process of rusting; it seems to play an essential part as an "exciter" in "setting-off" the reaction, by creating a galvanic current. Free hydrogen ions are known to be extremely active catalytic agents: we will return to this subject later.

The action taking place in corrosion by electrolysis may be written as follows:



HO is decomposed at the negative pole and hydrogen is precipitated; FeO is oxidized at the positive pole to form rust.

In the above formula the solution of the iron is shown as being due either to the action of impurities in contact with it, intensified by the contact-effect of the nascent hydrogen given off, or else entirely to the action of the hydrogen when the impurities are positive to the iron. If the impurities are positive, the hydrogen is given off at the surface of the iron and, as Dr. Walker says, charges the solution negatively. The fact of a metal being positive to an electrolyte in which it is immersed is the cause of its electrolytic (galvanic) solution, in accordance with Ostwald's Table, and solution will proceed until the negative charges carried by the ions of the metal into the electrolyte have accumulated to the point of counterbalancing the positive charges on the surface of the metal. This counter-potential is, necessarily, proportional to the osmotic pressure, both depending on the concentration of the ions in solution.

That the operation of rusting is of an electrolytic nature was very beautifully shown in the experi-

ments suggested by Dr. W. H. Walker and carried out by him in collaboration with Dr. Cushman.<sup>19</sup> A "feroxyl" reagent was prepared by neutralizing a hot solution of gelatine with 1/100 normal potassium hydroxide, using phenolphthalein as indicator, after which a few drops of a dilute solution of potassium ferricyanide were added. The pieces to be tested were immersed in this preparation, which solidified on cooling, incasing them; diffusion being retarded by the colloidal nature of the medium, local discolorations were expected to indicate the progress of chemical action. In these experiments the development of hydroxyl (HO) ions at the negative poles was shown by a pink coloration due to organic anions from the phenolphthalein, and at the positive poles the solution of the iron was shown by the blue coloration due to the ferrous cations.

In these tests it was found that, as a rule, the ends of the test-pieces were positive, giving rise to a blue coloration indicating ferrous ions, and rust was formed; at the central part where the pink coloration developed, the ions remained bright. The photographs published show nails which have their positive poles situated at the head and in most cases at the point also; this suggests that the compression of the head by upsetting and the squeezing of the end between the cut-off dies when the point is formed, resulting in an overstrained (crystallized) condition of these parts, may account for their positive polarity. After a while

there would take place a complete reversal, the positive and negative poles changing places until a further reversal brought back the original conditions, and so on continuously; in this way the different parts of the test-pieces rusted alternately.

The change of polarity is no doubt due to the formation of rust which would in time change the potential of the positive nodes in relation to the negative nodes. That after the first reversal a balanced system is not reached when there is an even coating—as far as the eye can judge—all over the pieces, might be due to an effect of persistence, similar to hysteresis, which would carry the action over the neutral point, as a fly-wheel carries an engine over the dead-center, but is more likely due to the very fact that rusting starting at separate points, there can be no coating really even in depth. Iron never becomes passive through rusting.

Dr. Cushman gives an excellent discussion of the relation of this electrolytic theory to the rusting of iron.<sup>16</sup> He shows that if a piece of iron or steel is immersed in water, positive and negative spots are established; according to his theory iron passes into solution at the positive spots and is converted into hydroxide, part of which piles up around those spots in crater-like formations, the rest migrating to the negative spots, where it collects in the form of cones. Microscopical examination readily verifies the presence of these craters and cones; we have here a plausible description of "pitting" which, whether on a small or large scale, always initiates

the process of rusting. Rust cannot take place unless negative and positive spots are established, the latter rusting first and continuing to do so until their polarity has changed; so much seems to be proven; hence homogeneity is the best insurance against corrosion; a speck of impurity will give rise to a positive annulus if it is negative to the iron surrounding it, and the iron will go into solution.

## THE SOLUTION OF IRON IN WATER

In 1822, Stodart and Faraday showed<sup>17</sup> that voltaic couples being present throughout the mass of commercial metals are the cause of these impure metals being dissolved more rapidly by acids than those which are of purer composition.

The resistivity of metals to acids is not, however, always an indication of the degree of resistance to corrosion. With a solution so weak that the action is no faster than in ordinary corrosion under severe natural conditions, the rates are probably about the same. To secure reliable data from acid tests, it is necessary to work with extremely dilute solutions, not exceeding 1 gram of acid per liter of water; the action is then too slow to be of practical service as a rapid test for corrodibility. In a later section some interesting tests by Gruner will be introduced.

The actual solution of iron by water, whether brought about by the voltaic effect of the contact between the metal and its impurities or by any other cause, is the crucial point of the electrolytic theory of corrosion. Whitney seemed to have proved beyond a doubt that iron is soluble in water,<sup>18</sup> and his results were confirmed by Miss Cedarholm and Bent, yet Dunstan and others failed to obtain any

solution whatever under apparently identical conditions; they therefore rejected the theories that hydrogen is evolved during rusting and that iron dissolves in pure water. Dr. Walker supported Whitney's theory of the solution of iron as positive ions; under the same conditions, in distilled water, it is asserted, that lead also will go into solution.<sup>19</sup>

To help solve the problem, Dr. Cushman devised a simple method<sup>20</sup> for testing iron and steel samples in water free from air and carbonic acid. In every case the metal remained bright, but rusted as soon as the air was admitted. To find out if iron did actually go into solution before the admission of the gases, a small amount of phenolphthalein was added; sooner or later it showed the presence of iron by its pink color. The smallest amount of iron which could be detected in this way would be .0004 gram, and it was claimed that the indicator, although itself a weak acid, could not account for the solution of the iron. If uniform confirmations of these results are forthcoming from equally reliable sources, the electrolytic theory of corrosion is proven, at least for ordinary iron, because in all these tests, while taking into account the composition of the medium, the experimenters apparently fail to take into account the minute variations which must have existed between the various so-called pure irons used. It may well be doubted if theoretically pure iron would dissolve in theoretically pure water, in which case the solution of iron, as observed by Cushman, would be due to the galvanic

action between the iron and its impurities, causing electrolysis of water, the hydrogen liberated then forming a couple with the iron, the latter being the positive and soluble partner. Dunstan and others may have experimented with an iron of greater purity than that used by Cushman.

Dr. Cushman explains Dunstan's failure to confirm Whitney's results, by arguing that by his method of operation he could not have had more than 0.000001 gram of iron in solution, and this would be too small a quantity to detect by means of the phenolphthalein indicator, and yet would be sufficient to induce corrosion. He concludes that the rusting of iron is due, not to a direct attack by oxygen, but by hydrogen ions; in fact, as will be shown later, oxygen may, under certain conditions, inhibit corrosion.

Dr. Moody describes how leaving old distilled water which had been well shaken up with air, in contact with a fresh polished surface of iron, during 40 seconds only, a weak solution of potassium ferricyanide detected iron in solution by its blue coloration, whereas when fresh distilled and unshaken water was used no iron could be detected.

The true cause of iron going into solution remains perhaps to be found, but consideration of the influence on corrosion of the many impurities present in iron and steel may, as just stated, lead to the correct solution. The subject will receive further treatment in a separate section, but the author's theory of the process of rusting, under the

most favorable conditions, may here be restated as follows: Voltaic action between the iron and its impurities, or, possibly, among the impurities themselves, causes hydrolysis, or electrolytic decomposition of the water. If the impurities are negative to the iron, iron goes into solution; if the impurities are positive, they themselves dissolve and the iron remains immune. The function of the *free* dissociated hydrogen derived from the water (as against *combined* hydrogen, to be considered later) is of a catalytic nature. The free hydrogen is negative to the iron, and by its contact effect causes its solution. The fact is, hydrogen and iron cannot exist in contact without creating a difference of potential.

If the impurities are positive to the iron, the solution of the latter is the *second* step in rusting; the decomposition of water to supply hydrogen ions is the first, unless these ions are supplied by other means, such as acids or occlusion. This free hydrogen must not be confounded with the molecular or gaseous hydrogen which is given off during the process of corrosion, which has less function than significance; it is as much an effect of the process as the rust itself.

The product of rapid electrolysis of water by an electric current is two atoms of hydrogen and one of oxygen; the slow reaction of rusting results, apparently, in the formation of an atom of hydrogen and one of hydroxyl; that a difference of this nature should exist is not surprising; as we have

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already seen, different rates of oxidation produce different oxides. Once the iron is in solution, it is oxidized by any free oxygen present.

With rise of temperature, the readiness of iron to oxidize increases. Hot iron decomposes steam, yielding an impure hydrogen and is oxidized; corrosion is brought about by a similar action, but very much slower, voltaic electricity taking the place of heat. The quicker the reaction, the higher the oxide. Very slow oxidation gives rise to  $\text{FeO}$ , which cannot exist permanently as such in the presence of oxygen. At high temperatures  $\text{CO}_2$  is reduced to  $\text{CO}$  in the presence of iron, which is then oxidized to  $\text{Fe}_3\text{O}_4$ .

## ACTION OF HYDROGEN AND OCCLUDED GASES

If there are negative impurities, other than hydrogen, in the iron or in contact with it, iron will go into solution, as already stated, and rust will appear and continue to form until these impurities are exhausted and provided, of course, the rust is removed to preclude its own contact-effect on the metal. With ordinary irons, therefore, the primary cause of corrosion may well be the impurities, but their action can hardly account for the rapid growth of the rust. The contact-effect of hydrogen has been suggested as the most potent factor, and the de Meritens process of artificial corrosion has been brought forward in confirmation thereof; in this process the presence of occluded hydrogen is essential to corrosion.

Graham found that iron cooled in hydrogen absorbed 46 per cent of its volume. Prof. John Perry in 1872<sup>21</sup> detected the presence of hydrogen in steel. Ledebur found 0.0017 per cent of hydrogen in a soft open-hearth steel. The electrolytic activity of hydrogen was pointed out by Roberts-Austen.<sup>22</sup>

According to Lenz, 45 per cent of the absorbed gases in iron may be hydrogen, the balance being

carbonic dioxide, carbonic oxide and nitrogen in about equal proportions. According to F. C. G. Müller,<sup>23</sup> about 67.8 to 90.3 per cent of the gas in steel is pure hydrogen.

In some more recent investigations by O. Baudouard,<sup>24</sup> the following percentage weights of gases were found in commercial iron:

	CO <sup>2</sup>	H	CO	N	Total
Wire, 0.5 m.m. diam.....	0.035	0.0032	0.047	0.0105	0.0957
Wire, 1. m.m. diam.....	0.035	0.0017	0.062	0.0042	0.1029
Sheet, 1. m.m. thick.....	0.012	0.0018	0.081	0.0042	0.0990
Bar, 10. m.m. sq.....	0.021	0.0056	0.180	0.0141	0.2207

It is a well-known fact that iron or steel containing occluded hydrogen, due to pickling in acids, is hardened to a considerable extent and quickly oxidizes while in that condition; thorough washing and neutralizing of the acid will not correct the hardness nor the readiness to oxidize. Gas occlusion by this method may, normally, reach 12 times the volume of the iron, proving that most of it must be alloyed or in a liquid or solid state. The greater proportion of this absorbed gas is hydrogen.

On the other hand, electrolytically produced iron, which is quite difficult to corrode, is hardened to a considerable extent by the absorption of hydrogen during its deposition. The hardness of electrolytic iron is 5.5, as against 4.5 for ordinary iron. According to Cailletet<sup>25</sup> it will hold as much as 250 times its own volume of hydrogen, and the alloy containing 0.028 per cent (by weight) of hydrogen will scratch glass. This absorbed hydrogen must be relatively pure, and while this may preclude electrochemical activity among the gases themselves

it can hardly have much bearing on the difference of behavior between it and pickled iron, when exposed to corroding agencies.

The hydrogen contained in pickled iron can be almost entirely baked out of it at a low temperature; not so with the hydrogen absorbed electrolytically. This tends to show that in the pickled iron, the gas is not so permanently or stably combined—if combined at all—as in electrolytic iron. Furthermore, the great volume of the gas taken in by the electrolytic iron shows that a very large percentage must exist in solution as an alloy with the iron. The co-existence of three states of matter has been supported by Graham, Wiedermann and Spring. While there may be just as much free dissociated hydrogen contained in the pores of both classes of iron and the tendency to rust from that cause may be the same, yet the larger amount of hydrogen-iron alloy in the electrolytic iron may resist corrosion much better than iron alone.

The quality of resistivity to corrosion is intimately connected with the rise in electrical conductivity which is brought about by the chemical union of hydrogen with metals. Hot iron when quenched in water absorbs hydrogen, and Richards and Behr<sup>28</sup> have found that the electrode potential was raised by 0.15 volt, the nature of the gas being apparently the same as that which is absorbed in the presence of nascent hydrogen and therefore by electrolysis. The hydrogen taken up by finely powdered iron reduced at a low temperature was

not found to affect the e.m.f.; we may infer that the physical conditions attending the production of this iron were insufficiently powerful to cause the alloying on which the change of e.m.f. seems to depend. Dr. Steinmetz finds that electrolytic iron has a very high hysteresis loss, but attributes it to occluded nitrogen.

From an examination of all these facts, it would appear that the increase of potential due to the alloyed hydrogen in electrolytic iron overcomes the effect, as an electro-negative catalyzer or otherwise, of hydrogen in a free ionic state only. In all classes of iron the hydrogen exists in both conditions, free and combined, just as carbon does in pig-iron, but the proportion of hydrogen-iron alloy in electrolytic iron is very much greater than in the other metals. Hydrogen, like carbon, when present in a free state will by contact action promote corrosion; like carbon, also, when chemically combined with the iron it will resist corrosion, but if the alloy is unevenly distributed the pure iron in contact with the alloy will be attacked.

According to Roberts-Austen, silicon, manganese and aluminium prevent the escape of hydrogen from iron; Ledebur claims,<sup>27</sup> however, that brittleness after pickling, due to hydrogen, is greater if the combined carbon is high, while silicon has the reverse effect; he is in accord therefore with Troost and Hautesfeuille,<sup>28</sup> who claim that silicon diminishes absorption. These seemingly opposite statements may be reconciled by assuming that, while silicon

may reduce the absorption of hydrogen, it will also retard its subsequent removal just as non-conductors which absorb heat with great difficulty will, on that very account, retain it the easier. Manganese is said<sup>28</sup> to greatly increase the absorption of the gas while diminishing that of carbonic oxide, which is, in any case, very slight. Manganiferous pig-iron retains more gas than does ordinary pig.

Pressure applied during the solidification of metals—as, for instance, in the Whitworth process—prevents the escape of the gases. They can be driven out by heating, preferably in vacuo, or locally by machining or drilling; the combination is, therefore, not a very close one. To drive the gases out of pig-iron, a temperature of 800 deg. C. is sufficient. Malleable iron contains more carbonic oxide than hydrogen and it is retained with greater energy. Steel is said to absorb somewhat less than cast-iron, and wrought-iron less than cast-iron; these differences are, in great measure, no doubt, functions of the porosity.

Occluded gases, and especially hydrogen, must not be lost sight of when dealing with the problem of corrosion. Hydrogen is the lightest and, therefore, kinetically the most active of elements; it seems to be in a way a sort of universal catalyzing “daemon,” an extravagant statement to the ear, perhaps, and decidedly questionable, but with some merit of suggestiveness; all chemical reactions take place in the presence of hydrogen, if only as a trace of moisture or of a volatile hydrocarbon, and

it is the only element of which this is true. Hydrogen, which seems to form the main ejection from the sun, and may be regarded as closest to the primordial element from which, according to recent well-grounded theories, all other elements may proceed, is unique in many of its properties; it seems to stand apart from the other elements in many ways. These differences are, in many cases, attributable to the great activity of its molecules in proportion to their mass, hence, for instance, the distinct character of its curve representing the value of  $p_v$  under different pressures.

The diffusion through a finely porous material which gives rise to dissociation is similar to, if not identical with, osmosis; in osmosis the porous membrane causes dissociation resulting in chemical effects which are the basis of important reactions and, among others, of organic growth and life.

Hydrogen will pass through platinum and red-hot iron (Ste. Claire-Deville) and its ready dissociation, which was demonstrated in Winklemann's important study of its diffusion through palladium,<sup>29</sup> suggests a belief in its breakdown, under conditions of common occurrence, into free and active atoms, ready to take the first opportunity offered of entering into a combination. The condition of most common occurrence is, as we have seen, the contact of dissimilar substances. The occlusion of free hydrogen in coal-dust, wheat-dust, zinc-dust and other dusts will go far to account for their detonation by spontaneous oxidation. These dusts act

in the same way as does spongy platinum on certain gases which it ignites by simple contact. Activity in all these cases is, in great measure, a function of the surface exposed, hence a porous metal is more readily oxidized than one which is solid. Whether or not the surface of iron may act as a porous membrane and aid dissociation is a matter for discussion.

According to a theory due to Hittorf, which may now be applied to the subject, when the solution has assumed a positive charge which counterbalances the negative charge on the surface of the metal, there is an arrest of solubility due to the formation of an "electrolytic double-layer," a sort of neutral film. If hydrogen ions are present, molecular hydrogen is precipitated, because iron is positive to hydrogen, or, as is often said, has a greater "solution pressure." The precipitated hydrogen carries positive electricity out of the solution; then the solution is supposed to try to make up for this loss by taking the positive element of the double-layer which is thus broken down, and solution of the iron proceeds.

The hydrogen is, necessarily, precipitated at negative points, either on the iron itself—which implies its being non-homogeneous—or on any negative substance which may be present, either in the solution or as a so-called contact substance. Copper, for instance, being negative to iron, will, by aiding the precipitation of hydrogen, favor the solution of iron. Rust has already been mentioned as hav-

ing the same effect. Concentration of hydrogen ions favor solution, hence the action of acids; concentration of hydroxyl ions inhibit solution, hence the action of alkalis.

As already suggested, the dissociation of water by the action between iron and its impurities will furnish the necessary hydrogen ions; occlusion of hydrogen (though not alloying with it) will have a similar effect. The theory of solution-tension, as an intrinsic property of iron, is perhaps superfluous; at any rate, its nature has received no rational explanation; we have no proof of its existence in the case of strictly pure metals immersed in strictly pure solvents, but we do know that it possesses a curve which points to  $^0$  for these ideal conditions.

The solubility of metals through local currents (Auren and Palmaer) due to impurities or variations in structure is readily understood.

It is really the same thing whether hydrogen occluded in a piece of pickled iron be said to increase solubility by breaking down a "double-layer" or by galvanic action which drives the iron into solution in the effort to restore electrostatic equilibrium; whichever way it is explained, the solubility is due to hydrogen giving iron a positive polarity; this polarity will cause its solution whether there be a neutral film or not—for, after all, a neutral film is equal to nothing. Whether the horse be put in front of the cart or behind it, the cart moves and the horse moves it; either way, the horse is the

cause and not the effect of the motion. So it is with hydrogen in corrosion; it is essentially a cause, although, as stated before, it may neither be the first nor the whole cause.

## THE FUNCTION OF OXYGEN

Under the title of "The Function of Oxygen in the Corrosion of Metals,"<sup>30</sup> Dr. W. H. Walker has contributed a most valuable discussion to the chemical literature of corrosion.

It is universally agreed that rusting requires free oxygen. Whatever theory of corrosion is adopted, one essential function of oxygen is to convert either Fe or FeO into  $\text{Fe}_2\text{O}_3$ , rust.

Dr. Walker lays stress on another function of oxygen, giving it, in fact, first place; this function is the removal of the layer of gaseous hydrogen which may accumulate on the surface of the iron and arrest further action. This is the well-known effect presenting itself in electric batteries and called "polarization." Oxidizing agents, known as depolarizers, will remove this film of hydrogen, allowing decomposition to proceed. As we shall see later, certain depolarizers, such as the bichromates of sodium and of potassium, between certain concentrations, have just the reverse effect; they inhibit rusting. The reasons for this will be fully discussed, but it may be well to state here that the effect of the chromates supports the theory that hydrogen is removed from contact with the iron

and even replaced by the dissociated oxygen, which is electro-positive to iron and protects it after its removal from the solution of the chromate, by bearing the entire weight of the attack by hydrogen. Electro-negative metals, such as copper and lead, act as depolarizers and hasten the rusting of iron or steel with which they are in contact.

That the removal of molecular hydrogen is a most necessary function of oxygen in corrosion is an important fact to remember. Oxygen having thus two functions, it is doubly important to heed Dr. Walker's plea for the removal of air from boiler-feed waters.

In the article already referred to, Heyn and Bauer draw the following conclusions, among others, regarding oxygen: 1. Free oxygen is necessary for rusting. 2. Iron is an extremely sensitive qualitative reagent for oxygen dissolved in water. 3. In an atmosphere of pure oxygen, rusting is three times as rapid as in air. 4. If air is bubbled through the water rusting takes place about twice as rapidly as when the air is merely in contact with the surface of the liquid.

### THE DIFFERENCE BETWEEN IRON AND STEEL.

The principal difference between iron and steel lies in the carbon content. Iron having over 0.04 per cent of carbon is usually called steel; if there is less than about 0.15 per cent it is known as a mild steel. Save in the arrangement and distribution of the constituents, it cannot be said that, chemically speaking, there is any sharp line of demarcation between iron and steel, but the processes of manufacture are different and the two metals have therefore different physical properties.

Steels, with the exception of the very mild ones, are susceptible to being hardened, and it is well to note that steels harden by changes in the carbides, whereas chilled iron is hard because of a change in the structure of the surface from crystalline to amorphous, or nearly so.

Carbon is present in iron and steel, either as microscopic flat crystals of graphite or as carbides of iron, of which a number of varieties are known, more or less distinct from each other. The most common one is cementite, a definite compound,  $\text{Fe}_3\text{C}$ ; pearlite, an intimate mixture of cementite and ferrite (pure iron) forms the bulk of most

steels, and martensite is the carbide produced by sudden cooling. Sulphur, phosphorus and silicon are present as sulphides, phosphides and silicides. Manganese, which is added as ferro-manganese in the process of manufacture to prevent the occlusion of gases, is always present either alloyed or in combination with the non-metallic impurities. In special steels there may be nickel, chromium, tungsten, molybdenum, vanadium, etc. If the impurities are not dissolved in the iron they will separate as eutectics; this will depend in great measure on the heat treatment and mode of cooling.

## THE STRUCTURE OF IRON AND STEEL.

The normal structure of iron and steel is crystalline; fibrous iron is a misnomer; the fibrous appearance is due to the way in which the crystals draw out from each other in the direction of their main axes when the metal is fractured. The more slowly and uniformly the heating and cooling have been carried out, and the less interference there has been by mechanical distortion, the more regular and small will the crystals be; these crystals always lie in the direction of the heat waves passing out in cooling; they are, therefore, at right angles to the contour planes of the piece; it is on this account that sharp angles are to be avoided in cast metal work, as they cause a sudden change of direction in the position of the crystals. When cast-iron is "chilled" it appears to be set in a more or less amorphous condition, hence its lack of flexibility.

A change in the crystalline structure of iron may be brought about by shock or continual vibration; the fracture becomes coarser and there is a simultaneous loss of strength; the iron is said to be crystallized. The strains which alter the mechanical condition of matter are: crushing, tensile, flexional or torsional. The factors governing variations in the

results will vary according to the moment of the strain, or its average intensity multiplied by the period during which it acts. The effects of strain will also vary in different parts of the same piece from differences in the original heating, lamination, forging or cooling which it may have undergone. Shearing, punching and other operations will alter the structure; the walls of a cold-punched hole are unfit for threading because they are disaggregated, hence they should be drilled or reamed out. Swaging, unless performed gradually and at very high speed, will have a tendency to crush the material and make it "short," whereas light, rapid swaging and drawing through dies will tend to interlock the crystals. If annealing is required after drawing wire and sheets, it is because the crystals are not as regularly and snugly packed by exterior mechanical means as they are by the crystallogenic forces which act during cooling from high temperatures. It is evident, then, that all manufactured goods must be more or less heterogeneous in their structure.

## RELATION OF STRUCTURE TO CORROSION

It is found that, apart from chemical and voltaic causes, corrosion will vary according to the structure of the material and the mechanical treatment to which it has been subjected. It is also known that metals in large masses will not corrode as rapidly in proportion to the surface exposed as will smaller masses of the same composition and in the same physical condition. The reasons governing these facts are still obscure, notwithstanding the many plausible theories which can be advanced.

Hard cast-iron is less corrodible than soft cast-iron of similar composition,<sup>31</sup> and it corrodes faster if cooled irregularly than if cooled uniformly and slowly. The inner portions, being more uniform in texture, corrode more uniformly and slowly (Mallet). The more porous the material, the more rapidly will corrosion proceed and the more deep and destructive will it be. Blowholes of any size invite rust. It has been found that iron gun-barrels corrode more rapidly in wet weather than those made of compressed steel (W. A. Adams). The part of a pipe along the weld, which has been somewhat compressed, in the closing operation,

does not rust as rapidly as the part opposite the weld. As first discovered by Kalischer, metals conduct electricity better when their structure is crystalline; an amorphous metallic foil which has been rendered crystalline by careful heat treatment will become a better conductor. Increased conductivity implies better resistance to corrosion.

The microscopic porosity of iron and steel has been shown and even measured by Thörner.<sup>32</sup> Under ordinary circumstances, water cannot pass through the pores and fissures in iron, on account of their capillary action, but a high pressure will overcome this capillarity, as shown in the "sweating" of hydraulic presses. The absorption of gases likewise proves the porosity of iron and steel. At high temperatures all metals absorb gases, losing part of them again upon cooling. As already stated, all manufactured iron and steel goods have to undergo some form of heat treatment and are found to contain hydrogen, nitrogen and sometimes carbonic oxide.

Carelessness of manufacture which tends to heterogeneousness is an invitation to corrosion and in itself goes far to explain why modern steel, which is tortured into shape at such a high speed that the molecules are not permitted to readjust themselves, is said to be more corrodible than the metals produced a generation ago; in those days iron was produced in small quantities, without the addition of other metals, and was rolled slowly and allowed to cool naturally. The internal strains due to me-

chanical treatment are not to be confounded with the unevennesses in the distribution of the impurities due to segregation in cooling; these mechanically induced strains are really equivalent to straining the metal beyond the elastic limit, which, as will be seen later, makes it more corrodible. Moreover, the tonnage-craze from which the quality of product in so many industries is to-day suffering, is causing to be placed on the market a great mass of material, only a small portion of which is properly inspected, which is not in proper condition to do its work—rails and axles which fail in service and steel skeletons for high buildings which may carry in them the germs of destruction and death.

## EFFECT OF STRESS ON CORROSION

"The effect of stress on the corrosion of metals" is the title of an instructive paper by Thomas Andrews, published in 1894,<sup>33</sup> in which the results of extensive electrolytic tests, tensile, torsional and flexional, made in saline solutions are recorded. In all classes of tests the results were of the same nature; the unstrained parts were, by galvanometer readings, shown to be electro-positive to the strained parts and hence more subject to corrosion. On the other hand, according to experiments made in France that same year, if iron and steel are strained beyond their elastic limit, the surface corrodes with greater rapidity along the lines of deformation, where molecular cohesion has been broken down and the metal been made more porous. The author's own observations of overstrained bolts confirm this view, and it is a well-established fact that the metal around punched holes will rust more rapidly than that around drilled holes, because the degrees of strain differ.

Dr. Chas. F. Burgess found<sup>34</sup> that in steel strained tensionally and torsionally to just below the point of rupture, the strained parts corroded very much faster than the unstrained; the unstrained ends

being cathodes, bubbles of hydrogen were given off from them under water. These results in no way invalidate those of Andrews; Dr. Burgess worked with pieces strained beyond the elastic limit, and they had undergone permanent structural deformation, whereas Andrews worked within the safe limits allowed by engineers, where no permanent deformation within a long period of time is to be feared.

In recent experiments made by E. Rasch<sup>35</sup> it was found that during tensile tests of brass and mild steel, within the elastic range, the metal became cooler, and beyond the critical point or elastic limit it became hotter. A loss of heat is to be expected during structural breakdown, and its connection with the change of electrical conductivity is evident. Some years ago A. Witkowski found<sup>36</sup> that in a strained metal there is an increase of electrical resistance in the direction of the strain.

All these observations go to prove the claim that mechanical treatment, by setting up uneven strains in different parts of finished pieces, will create variations of potential which will promote rusting. Whatever the composition of the different inner parts of the metal may be, and apart from any action which may be due to difference of composition, if there is a difference of molecular aggregation, it will promote the rusting of one or other of those parts. Action, power, everything knowable depends on difference of potential, and any chemical or physical difference between two por-

tions of matter in contact must give rise to a difference of potential and a flow of electricity.

If straining a metal below its elastic limit by exteriorly applied mechanical means will make it electro-negative to the same metal unstrained, the strains set up by chilling or hardening should have a like effect; the metal should resist corrosion to a greater extent and promote the corrosion of more positive metals in contact with it. This is found to be the case. Eighty years ago Daniell observed that a certain steel was dissolved by hydrochloric acid five times as rapidly when unhardened as it did when hardened; this is an indication of what we may expect with the agents of corrosion. Prof. Chas. E. Munroe<sup>37</sup> mentioned the case of a cold-chisel, tempered at the end, which had been dropped into an engine-room channel-way of the S. S. Triana in 1874; when found, some years later, the hardened part was not corroded, but the soft part was, and especially so at the line of immersion in tempering, which was clearly defined; at this point the contact-action was, of course, most pronounced; had the chisel been hardened throughout, it would, no doubt, have rusted all over; as it is, however, the soft part protected the tempered end, just as zinc will protect iron under similar circumstances.

"What becomes of the energy of a coiled watch spring when it is dissolved in acid?" is supposed to be one of the many unsolved mysteries of Science. The energy of the coiled watch spring is indicated by a slight shift of its potential towards the nega-

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tive end of the electro-chemical scale, resulting in an increase of e.m.f.; when the spring is put in acid, the energy is expended in retarding the action of the acid and is equivalent to a drop of temperature which would restrain chemical action. The energy of the spring, as increased e.m.f., counteracts the energy of the acid; it is expended and disappears as work of a negative character.

## COMPARATIVE CORROSION OF IRON AND STEEL

From a theoretical standpoint, steel, being negative to iron, should be the least corrodible of the two. As a general thing, results of tests between iron and steel have, in the past, resulted in favor of the iron; in most cases, the experimenters were undoubtedly looking for the defeat of the new material, steel, and their state of mind helped them to find it. Some of them were iron manufacturers who had much to lose by the adoption of steel. There are, however, a large and ever increasing number of contrary observations recorded, especially where the tests have been carried out with qualities of recent manufacture. The opinion one is led to form from a careful examination of recorded observations is in agreement with that of Ewing Matheson,<sup>38</sup> namely, that properly protected steel and iron rust to about the same extent, the steel doing so more uniformly; this is, of course, subject to the variations of structure already referred to, and those of chemical composition, especially as regards metallic impurities, which will be considered later, and limited by the fact that, undoubtedly, the best quality of charcoal iron is practically as resistant as the best qualities of steel used for similar purposes.

An important paper was presented before the Institution of Civil Engineers in 1881 by David Phillips,<sup>39</sup> "On the comparative endurance of iron and mild steel when exposed to corrosive influences"; excellent tables are given, and the general conclusions favor iron.

It must be borne in mind, as a limitation to all results adduced, that, while the initial rusting may be greater with either material, iron or steel, the rates of progression may be different and may bring about a complete reversal in the final result; the material which rusted faster at first may outlive the other. This is especially apt to be the case with forged, rolled and drawn metals, which are protected by a dense skin. Future tests should, therefore, either be carried out to destruction, as advocated by Howe, or else to the point at which failure of the material in service would result from loss of useful area.

A distinction must be made here between the cast and wrought metal: cast iron will not rust as readily as wrought iron unless the skin is removed, in which case it will rust faster. Rough and machined castings act quite differently.

The most radical difference between wrought iron and steel is the slag, which is always present in the iron; while this slag may protect the metal immediately beneath it, its contact effect on the exposed iron surrounding it must more than counterbalance this slight advantage.

The effect of slag has been the cause of much discussion. Some claim that wrought iron is composed of bundles of fibres, each of which is encased in slag. This theory implies that at the temperature of puddling, slag is able to distribute itself throughout the metal as a film of infinitesimal thickness. As Speller states,  $1\frac{1}{2}$  parts of cinder are expected to protect 98 parts of iron; further doubt is thrown on this theory by the fact that when wrought iron is examined under the microscope "the cinder is very irregularly distributed in strings and patches."

The author has tried the effect of breaking down this siliceous barrier by means of hydrofluoric acid. The test pieces were short lengths of wrought iron pipe of a well-known make. The acid solutions were normal and used in the quantities shown in the table below; in two sets of tests one-tenth the volume of normal hydrofluoric acid was added. In each case there were four test pieces, each piece being treated in a separate vessel. The weights in grams and percentage losses were as follows:

Test.	Weight 4 Pieces.	Scaling 2 hrs. 60 c.c.	Pickling, 20 hrs. 120 c.c.			
			I	II	III	IV
$H_2SO_4$	118.32	2.12 % loss	11.0	14.9	14.5	11.6 % loss
			12.9	26.0	36.7	47.3 total % loss
HCl	117.93	2.37 % loss	11.4	13.7	15.6	13.9 % loss
			13.5	25.4	37.0	48.8 total % loss
$H_2SO_4$ and HF	119.08	2.25 % loss	12.9	13.3	16.0	13.2 % loss
			14.8	26.3	38.0	49.5 total % loss
HCl and HF	118.26	2.35 % loss	12.3	13.1	16.3	15.4 % loss
			14.4	25.7	37.7	50.8 total % loss

On the theory of slag-covered fibres, a great increase in the solubility of the iron might have been expected, but such was not the case. From the appearance of the pieces after each test, it is evident that the hydrofluoric acid dissolved the slag yielding a smoother surface. Taking into consideration the very obvious mechanical protection of the iron by the undissolved slag in the case of the  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  by themselves, it seems remarkable that the differences were not greater.

According to another line of argument, the silicates exist in streaks and form a sort of "fence," an almost perfect barrier against the agents of corrosion, say the Ironites; wide open to those agents, say the Steelites; to the argument of the former that "steel has no fence," the latter might reply that it needs none, being a wall in itself.

While the presence of slag may be the most radical difference between the two metals, the most important one for the present discussion is the difference between the amount and composition of the carbides of iron.

The carbides of iron have a greater specific heat than iron itself; this implies a high resistance to corrosion; the difference varies directly as the carbon content and is, according to Meuthen,<sup>40</sup> 0.0011 for each 0.5 per cent of carbon. According to these investigations, the specific heat of cementite is 0.1581, whereas that of ferrite is 0.1432; these values check up closely by Kopp's law of molecular heat. A galvanic current must be created by con-

tact of the carbides and the ferrite. A steel containing about 1 per cent of carbon is practically a compound of carbon and iron; it is said to be "saturated"; it is a most intimate mixture of ferrite and cementite, known as pearlite; on this account it does not pit readily; if by quenching from a high heat it is converted into austenite or martensite, this tendency is further inhibited. The author has found that in the case of two identically similar disks of steel, cut one after the other from the same bar, one of them being hardened, but the other left soft, and exposed together for about two years to ordinary agencies, the unhardened disk had 69.1 per cent of its surface corroded, whereas the hardened disk had only corroded over 56.8 per cent of its surface; the difference is not great (20 per cent), but it should be mentioned further that the rust on the hardened disk was of a darker shade than that on the unhardened disk, indicating a difference in the nature of the corrosion.

Prof. H. M. Howe offers the following suggestion<sup>41</sup> for a line of investigation calculated to produce a steel more resistant to corrosion:

"Perfectly pure metals are, in general, attacked by chemical reagents relatively slowly. The presence of any substance in them which does not dissolve completely in the metal, but gives rise to a new component, like the cementite of steel, accelerates solution, and corrosion is only a form of solution by difference of potential. The difference of potential is most effective, and hence the activity

of dissolving is greatest at the surface of contact of the two dissimilar constituents. From this we should naturally expect that, with a given quantity of any foreign constituent, such as cementite in steel, the finer grained the structure is the more rapid would the solution be, because the extent of surface of contact between the two will increase with the fineness of division.

"From this one may reasonably infer that those kinds of heat treatment and mechanical treatment which tend to leave the cementite in steel in the largest possible masses and herewith the smallest possible surface, will tend to retard corrosion.

"The cementite in steel actually exists in the form of fine particles mixed up with the iron in the form of pearlite. If my idea is correct, then the coarser the pearlite is and the less it is drawn out by mechanical work, the less rapid should be the corrosion.

"The inference from this would be that steel or iron which is to resist corrosion well ought to be finished at as high a temperature as possible, so that the particles of cementite in the pearlite may as far as possible coalesce and have the minimum surface of contact with the ferrite which encloses them.

"Experiment alone could show whether this inference is correct. Of course other and unforeseen conditions may nullify the effect of the coarseness, which is here pointed out as a condition tending to retard corrosion. For instance, it might turn out

that cementite in a fine state of division might act more effectively as a mechanical barrier to the progress of corrosion than the same cementite in coarser particles."

Prof. Howe's point is well taken. It agrees with the observation of Heyn and Bauer<sup>42</sup> that when overheated and non-overheated metal of identical compositions are placed in contact in water, the non-overheated metal is more strongly rusted than when placed therein alone, and protects the overheated metal.

In low carbon steels the distribution of the pearlite must be in scattered masses, and its effect must be similar to that of slag in iron; by its very nature, however, and on account of the high heat at which the metal is worked, the carbide can distribute itself more evenly than slag and this is readily seen through the microscope.

Iron contains very little carbon; it is therefore a loose mixture of ferrite and carbides; there are spots of carbide scattered about, because there is not enough carbon to permeate the mass throughout and form an alloy, as in the case of steel; each particle of carbide is a center for the promotion of rust.

With its report to the American Society for Testing Materials in 1908, the Committee on Corrosion presented a table<sup>43</sup> showing the rate of solution of different classes of iron and steel in a 20% solution of sulphuric acid applied during one hour. While a test of this nature is entirely worthless as

a test for corrodibility, the following general analysis of the results may be of some interest.

The wrought irons and Bessemer steels dissolved the most rapidly, one sample of wrought iron out-distancing all others. Charcoal-iron, steel muck-bar and wrought iron puddled plates followed in that order. Open-hearth steels and the high silicon, low carbon steel known as "ingot-iron," were the least corroded. Among the special steels, most of which resisted the acid far better than ordinary steels, nickel-steel easily led, followed by chromium and vanadium in that order.

Gruner has furnished some very definite data<sup>44</sup> on which to reject the acid test for all but special cases. His test plates, 28 in number, were fixed in a wooden frame during immersion. The results may be summarized as follows:

*In Moist Air:*

Chrome steels—Worst corroded.

Carbon steels—

Tungsten steels—Least corroded.

Gray cast-irons—Less than the steels.

White cast-irons—Less than the gray.

*In Sea-Water* (action reversed almost throughout):

Hardened steels—Less than annealed steels.

Soft steels—Less than manganese and chrome steels.

Tungsten steels—Less than carbon steels.

Gray cast-irons—More than steels.

White cast-irons—More than gray.

In a 0.5% solution of sulphuric acid the action was very similar to that in sea-water, the very mild steels and the high-grade charcoal-irons being, however, among the least corroded.

Gruner concludes that the acid test is worthless as a criterion for corrosion in moist air. The general conclusions from the above results would appear to be that in air steels are more readily corroded than cast irons, whereas the reverse is true in sea-water and in other good conducting mediums in which homogeneity is of greater account.

J. S. Unger<sup>45</sup> gives some interesting information about recent tests carried out by the Carnegie Steel Co.:

"We used three varieties of wrought iron, two of basic open-hearth steel, one of Bessemer steel and one of nickel steel. We subjected them to various agents, such as sea-water, 10 per cent solution of boiling brine, 1 per cent solution of sulphuric acid and 1 per cent of ferrous sulphate, made to imitate a mine water, and the action of ordinary well water, or water that contained no free sulphuric acid, but contained carbonates and sulphates of lime and magnesia.

"We found after treating them in the solvents for about a year the actions ranked in about this order: Common pipe wrought iron was corroded the most, then a medium quality wrought iron, followed by a low-carbon Bessemer steel; then by the best grade of wrought iron, then by open-

hearth steel, each of the open-hearth steels being corroded to about the same extent. The material that was least corroded was open-hearth nickel steel. Our object in testing the open-hearth steels was to determine whether open-hearth fire-box steel of high or low manganese would show a difference in corrosion.

"The plates under examination carried about 0.22 and 0.60 manganese. In the tests they were subjected to we found very little difference. The carbon, phosphorus and sulphur contents were about the same in both plates, the difference being in the manganese. Further experiments along this direction led me to believe that the more impure the substance the more rapid the corrosion, or, in other words, the Bessemer steel will corrode more rapidly than open-hearth steel; an acid open-hearth steel will corrode more rapidly than a basic open-hearth steel.

"We have found that in almost all cases the wrought iron will corrode more rapidly than steel. We have also found that on comparing high and low carbon steels made by the same process, such as high and low Bessemer or high and low basic open-hearth steels, that the higher the carbon, other things being equal, the more rapid the corrosion."

As regards the last sentence, it seems evident that in a low-carbon steel the higher the carbon the more numerous the centers from which corrosion may start, the steel not being saturated, being, in fact, a mixture of iron and iron carbides and non-

homogeneous. The low carbon content and freedom from cinder explain the qualities of the dead-soft open-hearth basic material used in America for making horse nails, which is misnamed steel.

Dr. K. F. Stahl finds that steel and iron tanks for storing sulphuric acid last equally well ; the steel corrodes more uniformly ; the iron is eaten out in streaks, which is no doubt due to the streaks of cinder rolled out in the plates.

## INFLUENCE OF MODERN CONDITIONS.

The prejudice existing against steel may be due to the changes in the conditions surrounding the use of iron and steel, especially the composition of the waste gases of combustion, which pollute the atmosphere, and the employment of electricity for lighting and transportation. To quote Prof. H. M. Howe:<sup>46</sup> "The fact that steel has come into wide use simultaneously with a great increase in the sulphurous acid in our city air and of strong electric currents in our city ground may well lead the practical man, be he hasty or cautious, into inferring that the rapid corrosion of to-day is certainly due to the new material of to-day, steel, whereas, in fact, it may be wholly due to the new conditions of to-day, sulphurous acid and electrolysis."

According to a recent analysis of freshly fallen snow at London, the atmosphere of that city is polluted by the following impurities—the quantities given are for one gallon of melted snow :

Solids (mostly soot).....	19.647	grams
Various soluble substances.....	0.780	"
Sulphuric acid.....	0.218	"
Sodium chloride .....	0.086	"
Ammonia .....	0.020	"

Sulphuric acid is purely an industrial impurity of the air; it and chlorine are among the most active known promoters of corrosion.

The prejudice against steel may also be due to the fact that, whereas the iron of some years ago was more homogeneous and freer from slag than the iron of the present day, the steel which is now manufactured is perhaps more homogeneous than that which was made during the early years of the industry, when only small masses were handled. In puddling, working on a small scale will give a better iron, freer from impurities, but in steel making, working on large masses of metal will, within certain limits, assist the diffusion of the components by maintaining the metal throughout at a more even and higher temperature for a longer period of time.

## CORROSION IN AIR

Iron will not corrode in air unless moisture is present, and it will not corrode in water unless air is present. This rule applies to salt-water also: R. Adie found<sup>47</sup> that corrosion did not take place in salt-water if air or oxygen was excluded, and that alcohol containing oxygen but no water would not cause corrosion.

Iron having a specific gravity of 7.8, produced in the laboratory, as against 7.3 for commercial pig-iron, is slightly oxidizable in moist air, but iron of a specific gravity of 8.14 produced in the electric furnace is scarcely at all.<sup>48</sup>

Of the agents present in the air which accelerate rusting, especially in or near cities where much fuel is consumed, sulphur dioxide and soot are the most destructive because together, in the presence of moisture, they conspire to produce sulphuric acid. The action is most marked in railway tunnels and bridges. Kent has studied the action of sulphur dioxide;<sup>49</sup> an analysis of sooty rust from a railway bridge showed the presence of sulphur dioxide, sulphuric acid, carbonic acid, chlorine and ammonia. Valuable papers on the decay of materials in tropical climates were published in 1864.<sup>50</sup>

## CORROSION IN FRESH WATER

The impurities in fresh water vary with the locality. Rivers flowing through industrial towns will contain hydrochloric and sulphuric acids and acids due to the decomposition of organic matter; all are highly corrosive.

Carbonic dioxide, air and excess of oxygen, all of which will accelerate corrosion, are present in all waters to a varying extent. Silica and alumina are without direct chemical effect. The variable impurities are as follows: carbonates of lime, iron and magnesium; sulphates of lime, potassium and magnesium; nitrates of lime and potassium; lastly, the chlorides of sodium, potassium and magnesium, which accelerate corrosion to a considerable extent. Salts which, like sulphates and chlorides, hydrolyze in solution to an acid reaction, promote rusting to a greater extent than when they remain neutral.

Water near the surface is more corrosive than lower down, because of the larger percentage of dissolved carbonic dioxide and air. Alternations of wetting and airing will increase the rate of corrosion, and on this account the most vulnerable part of a ship's hull from the outside is that part

known as the wash-space; continuous immersion is less destructive.

All and any impurities in water will accelerate corrosion; if the rule of uneven composition promoting the corrosion of iron is true, it must apply to the medium also. A heterogeneous medium must, necessarily, be the seat of voltaic currents, the effects of which would be to supply the hydrogen ions required to promote corrosion.

In the case of iron-work at the mouth of a river, where the water is brackish, strata of different degrees of salinity are to be found; on this account the rate of corrosion is particularly rapid at the point where the water is most salty; it is, on a large scale, the effect suggested as taking place in each drop of every non-homogeneous medium.

Rain water is relatively pure, but even it will contain salts dissolved from the dust in the air, which increase its conductivity and rusting properties. Theoretically pure water would be a non-conductor and could not, therefore, serve as the electrolyte in the process of rusting.

## CORROSION IN SALT WATER.

In sea-water the proportion of chlorides is very much greater than in fresh water; moreover, some ammonia and the bromides of magnesium and iodine, all of them powerful aids to corrosion, have to be reckoned with. Sewage, which is almost always present near the mouth of rivers, supplies sulphates, nitrates and organic matter. According to records, the most salty seas are the Mediterranean and Dead seas, and the least salty are the Baltic and the Black seas.

Saline matter in water decomposes in contact with iron which fixes the negative elements; it also serves to increase the conductivity of the water considered as an electrolyte and, as already suggested, increases the heterogeneousness of the medium, resulting in galvanic action in the medium itself which may supply hydrogen ions. The most extensive and complete investigation of the action of sea-water on the metals of ships is due to Robert Mallet,<sup>51</sup> and he has published some very important tables.

When cast-iron is left in sea-water for a long period of time it undergoes a remarkable change, being converted into a pseudomorphous mass of a

black substance resembling plumbago. As far back as 1822 it was known that slightly acidulated water would have this effect on iron, and 40 years later Dr. Calvert found this to be the case with salt-water also. Guns from the wrecks of the Royal George and the Royal Edgar, which had been under water 62 and 133 years, respectively, were found to have become black and soft, so that they could be cut with a knife, and when brought up into the air they absorbed oxygen so rapidly that they heated up. They must have been extremely porous. Cast-iron pipe used for conveying salt-water has been known to undergo the same transformation.<sup>52</sup> A piece of an iron ship's heel-post, which had suffered considerable decomposition of this nature, was found by David Mushet<sup>53</sup> to be of the following composition:

Carbon dioxide and moisture.....	20.0	per cent.
Protoxide of iron (FeO).....	35.7	"
Silt or earthy matter.....	7.2	"
Carbon .....	41.1	"

The FeO and CO<sub>2</sub> were no doubt present mostly as Fe<sub>3</sub>O<sub>4</sub> and FeCO<sub>3</sub>.

Mallet attributes the conversion of the iron into a plumbago-like mass to the action of the carbonic dioxide present in the water.

Some tests were made in 1882 by J. Farquharson<sup>54</sup> on six plates of iron and six of steel; these were immersed for six months in Portsmouth Harbour, six of each separately, the other six as connected couples; in this way the comparative corrosion of the iron and steel was obtained and also

the increase of corrosion due to galvanic action between steel and iron. The following table gives the losses observed in ounces and grains:

(a) Steel	{	in contact.....	0-427
Iron			7-417
(b) Steel	{	separate.....	3-340
Iron			3-327
(c) Steel	{	in contact.....	0-297
Iron			7-770
(d) Steel	{	separate.....	4-000
Iron			3-190
(e) Steel	{	in contact.....	2-337
Iron			6-000
(f) Steel	{	separate.....	4-157
Iron			4-570

These results, which were confirmed by Mr. W. Denny from his experience in the case of the S. S. Ravenna, are interesting to analyze. They show that in two cases only did the steel corrode to a greater extent than the iron, but the difference is so slight that for all practical purposes it can be said that the steel and iron of the experiments (ship-plates) were equally affected. They also confirm the theory that the combination of steel and iron, which is quite frequent in practice, is detrimental to the iron, but protects the steel, which is the negative partner. They also throw light on previous observations and lead to the conclusion that good homogeneous iron and steel are about equally corrodible. As we shall see later, the most valuable advantage which steel possesses over iron is due to the fact of its not pitting so deeply.

Iron in contact with non-metals will also suffer from galvanic action, as shown in the case of a bolt which was corroded almost entirely through at the junction of pieces of elm and pitch-pine, which it held together,<sup>55</sup> and the case mentioned by Matheson of a piece of iron on a bridge which was corroded to a knife edge where it came in contact with wood.

The effects of electrolytic action are clearly demonstrated by the results secured by Mallet in a series of experiments which he undertook in order to ascertain the "amount of corrosion in equal times in clear sea-water of a unit surface of wrought iron plate exposed in electro-chemical contact with an equal surface of the following metals electro-negative to it, as compared with the corrosion of the same surface of the same iron exposed alone for the same length of time":

	Relative Corrosion.
Iron plate alone.....	8.63 per cent.
In contact with: Brass ( $\text{Cu}_2 + \text{Zn}$ ).....	29.64 "
Copper .....	42.79 "
Lead .....	47.90 "
Gun-metal (Bronze).....	56.39 "
Tin .....	74.71 "

In connection with the above table, the valuable fact is mentioned that the brass alloys of composition  $\text{Cu}_8 + \text{Zn}_{17}$  to  $\text{Cu}_8 + \text{Zn}_{18}$  are without galvanic action on iron in sea-water. The alloy of iron, copper, zinc (and sometimes tin), which is known as Delta Metal, tested under similar con-

ditions with wrought iron and steel, showed remarkable resistance, as follows:<sup>56</sup>

	Wrought Iron	Steel	Delta Metal
Loss .....	45.9	45.45	1.2 per cent.

The first copper-zinc alloy for the special purpose of resisting the action of sea-water was patented in 1832 by G. F. Muntz. Muntz Metal is used for bolts, valves, etc., and for sheathing ships; its composition is 2 parts zinc to 3 parts copper. Tobin bronze is similar to Delta Metal, but contains tin and lead.

According to Heyn and Bauer,<sup>57</sup> cast iron protects wrought iron in contact with it, and contact with nickel will increase the rate of corrosion of iron from 14 to 19%. The same investigators found that iron in contact with copper rusted 25% faster in ordinary water and 47% faster in sea-water.

The interior of ships is subject to various agents of corrosion. At certain points the temperature is higher than at others, and escaping steam keeps the atmosphere moist; the bilge-water also is of a highly corrosive character; the coal abrades the sides of the vessel, holds moisture in contact with them, and induces the formation of sulphuric acid if sulphur dioxide is present, besides, coal is, in the presence of sea-water, strongly electro-negative to iron. Some cargoes and the fermented or decaying remnants of old cargoes are likewise aids to corrosion. Cement is used for coating ship-plates on the inside, but this prevents examination of the hull, and it is porous to moisture and gases.

## CORROSION OF RAILS

The case of steel rails is an interesting one, showing as it does the effect of vibration on rusting. A rail which has been in service but has been laid to one side will rust all over, but especially at the ends where the vibration of the fish-plates has removed the mill-scale, and on the smooth top of the head. On the other hand, a quite remarkable fact, which has been universally confirmed and can be easily observed by any one, is that a rail while in service will not rust nearly as rapidly as one which is lying out of service. The rusting takes place in proportion to the service, and lines over which fast trains pass frequently, causing much vibration, will practically not rust at all, whereas the rails of turnouts or sidings, which undergo less service, and that of a slow nature, will rust to a certain extent. One observer (J. M. Heppel) has reported the case of some rails at Madras, India, which lost 3 pounds to the yard lying in the yard exposed to the sea air, while the rails in service nearby were not perceptibly affected.

The top of a rail is compressed and smoothed down in service by the grinding of wheel tires, for there is always a certain amount of slip, especially

during acceleration and retardation. Galvanic action between the smooth head of the rail and the rest of it has been suggested to explain this immunity from rust, but it is not at all likely that the foot would owe its protection to the thin stratum of denser metal so far removed from it. If that dense skin on the top of the rail were not crushed beyond its elastic limit, it would, on the contrary, tend to accelerate the corrosion of the steel in contact with it.

The real reason for this difference of behavior seems to lie in the observed fact that oxidation is apparently arrested, or at least greatly retarded, by vibration.<sup>58</sup> Explanations seem to stop at this point, but a simple theory can be built on the assumption that the vibration causes a shedding of the rust as soon as it is formed on the spots that are not protected by mill-scale, and there is, therefore, no acceleration of the action due to the accumulation of spongy and electro-negative rust. The average speed of corrosion of a vibrating body would be that of the formation of a first film of rust. Most of the actual rust on rails is probably due to the rapid evaporation of rain on the surface. In the case of rails in service, the first film of rust would be confined to bare spots and cracks in the mill-scale, and the vibration would prevent its working its way under the mill-scale, as would happen if the rail were at rest.

The top of the rail being denser might be expected to resist corrosion better when the rail is

out of use; such is not the case, however. The surface has not only been subjected to hammering and crushing, but also to abrasion and rolling, and it has become short and crackled and sometimes exfoliated; once laid aside, the smooth top of an old rail rusts very rapidly.

## CORROSION OF TUBES

The carefully acquired experience of the largest manufacturers of tubes in the world, which induced them recently to abandon the manufacture of wrought iron pipes, teaches that the use of steel in place of iron—at least in the United States—for the special purpose of tubing, is to be preferred; the tendency of the steel to pit is somewhat less than that of iron, and it welds at the joint fully as well.

The joint investigations of H. M. Howe and Bradley Stoughton confirm these results. It must be borne in mind that the conclusions apply to skelp material only. They are further corroborated by experiments recently made by T. N. Thomson,<sup>59</sup> who finds that iron and mild steel pipes corrode about equally, the steel having, however, the advantage in the all-important matter of pitting. In a test of three pieces of wrought iron and three pieces of mild steel pipe conveying hot water during about one year under conditions identically the same, the iron pipe lost by rusting  $20\frac{3}{4}$  ounces in  $9\frac{13}{32}$  pounds (13.4 per cent), and the steel pipe  $24\frac{7}{8}$  ounces in  $9\frac{11}{32}$  pounds (15.6 per cent). The experimenter did not stop short at these figures

and argue therefrom, as all his predecessors had done, that the steel pipe was inferior to the iron pipe as a merchant article, although evidently slightly more corrodible; he estimated the degree of pitting by averaging the measured depth of the five deepest pits in each piece and thence he calculated the number of days the pipe would remain sound and not show a leak; there is no evidence of his having taken into consideration the fact that the internal pressure would cause a leak before the metal was pitted through; however, the proportions, as shown in the following table, would hold good:

Steel 850.4 days	Iron 780.5 days
780.5	759.7
759.7	686.5
Average..... 796.9	742.2

The steel pipe was therefore 54.7 days, or  $7\frac{1}{2}$  per cent, more durable than the iron pipe. Hot-galvanized pipe was found to last about 20 per cent longer than the ungalvanized; this result, applying to a few pieces of similar origin and tested under conditions where galvanized pipe is unsuitable, is of little value. If it were correct, galvanizing would not justify its cost.

Mr. Thomson also draws the following conclusions from a large number of observations collected from all parts of the United States: That in the case of pipe buried in the ground and conveying steam or hot water, the exterior corrodes rapidly, but when the pipe is not buried, and unless air and other gases be removed from the water, the interior is corroded more rapidly than the exterior.

The tests of Howe and Stoughton and the evidence which they have collected is of great interest. Of ten different tests made by different observers in different places, seven resulted decisively in favor of steel; in the other three cases the results were very slightly in favor of the iron, but in only one of the latter was the material of modern manufacture. The tests which resulted in favor of steel were as follows, all except the two first being carried to destruction: Seven months in hot, aerated salt-water; sixteen months buried in dampened ashes; exposed to sulphuric acid coal-mine water; in railroad interlocking and signal service; in locomotive boiler service. It was also found that steel tubes made in 1906 pitted much less than those of 1897 from the same makers, indicating the superiority of modern steel over that of some years back in this particular respect.

In 30 complete service tests made by railroads during the years 1907 and 1908, modern steel tubing showed a slight superiority over so-called charcoal-iron tubing and the rusting was more uniform.<sup>60</sup>

Badly made steel will evidently corrode faster than a uniform product, and the question of the comparative corrosion of iron and steel should not be judged from the behavior of a poor quality; unfortunately, persons afflicted with mental hustling always generalize exceptions.

F. N. Speller has invented a process of mechanical working or kneading of the surface of the metal

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for tubes during rolling which has been found to improve its texture and render it more uniform; the process is known as "spellerizing" and is now in extensive use. In the following table of corrosion tests<sup>61</sup> Nos. 4, 5 and 6 were on spellerized steel. Results are shown as percentages of corrosion, as compared with iron:

No.	Conditions	Authority	Duration	Iron	Steel	Test Started
1	Aerated dist. water, normal temperature	U. S. Navy	64 weeks		94.5	1901
2	Sea water, normal temperature	H. M. Howe	2 years	100	119.0	1897
3	Aerated brine, normal temperature	Nat. Tube Co.	6 mos.	100	106.0	1904
4	Aerated water, 180° F.	Nat. Tube Co.	3 mos.	100	90.6	1906
5	Aerated brine, 180° F.	Nat. Tube Co.	3 mos.	100	75.3	1906
6	Aerated sea water, 180° F.	Nat. Tube Co.	3 mos.	100	94.2	1906

The value of the proofs adduced in defense of steel pipe has been seriously questioned, and, with perfect justice, it has been pointed out<sup>62</sup> that the value of short as against long time service tests is a most important one. In the case of steel and iron pipes put in service 20 years or more ago, the iron pipe has, in all known instances, resisted corrosion far better than the steel; in recent short service tests and laboratory tests the steel has almost invariably won. The difference may reside in the fact that modern steel does not pit as readily as the

steel of some years ago, because it is more homogeneous, as indicated by its improved tensile qualities.

The Riverside Iron Works found that iron boiler sheets corroded faster than steel sheets when buried in soil which was kept moist with a solution of carbonate of soda, nitrate of soda, chloride of ammonium and chloride of magnesium, which are among the most active corroding substances commonly found in water; the results were as follows:

After 23 days	Iron loss.....	0.84	per cent.
	Steel " .....	0.72	"
28 days later	Iron loss.....	2.06	"
	Steel " .....	1.79	"

Boiler tubes in service will suffer severely if exposed to the action of fatty oils which, even if perfectly neutral, have a strongly corrosive action on iron in the presence of steam.<sup>63</sup> Cottonseed oil, which is used as an adulterant of cylinder oils, must be avoided. The great enemies of boiler tubes are, however, the sulphuric acid and salts in the feed-water and dissolved oxygen. The former can generally be taken care of by the use of certain compounds or by other chemical means, but the latter is more difficult to remove and demands special study. Zinc is only of value in boilers if the water is in the condition of an electrolyte, hence, while good for marine boilers, it is of little or no use in fresh-water boilers.

### CORROSION OF WIRE AND SHEETS.

In the case of wire, the consensus of experience seems to be just the reverse from what it is with pipe. In his report on "The Corrosion of Fence Wire,"<sup>64</sup> Dr. Cushman quotes the opinion of a concern which is a very large consumer of wire, that "Bessemer or mild steel wire will rust or deteriorate much more rapidly than iron wire. In all probability, three times as rapidly." He also found that, according to the unanimous opinion of farmers, modern steel wire fencing is much more corrodible than the old iron wire. It is difficult to see why there should be this reversal of properties for wire as compared with tubing, in view of the fact that steel wire has a harder skin than iron wire, because, being less malleable and being harder to draw through the dies, the packing of the material at the surface is more marked. This is easily proved by treating pieces of steel and iron wire with an acid; the acid eats out the metal on the ends according to its degree of porosity, and it is found that the steel wire shows a denser and better defined skin than the iron. In the case of iron, the honey-

combing extends much closer to the edge. The skin seems to resist the action of the acid in the ratio of its density. The same effect of acids may be observed with all rolled material, notably sheets. In its investigations, the Division of Tests of the Department of Agriculture found, as would naturally be the case, that modern steel wire was, on an average, much higher in manganese than the old iron wire.

One might almost think that in the case of *thin* material the results are the very opposite of what they are with heavy material. This may be due to the repeated pickling and drawing or rolling, causing cinder to accumulate at the surface in sufficient proportion relatively to the iron to form a protective layer. The condition of the surface of iron wire and sheet after it has been etched would tend to confirm this view.

As regards sheets, the published records would indicate the superiority of iron over steel, but, as in the case of tubes, the relation may be shifting. A recent reliable service test of unprotected roofing sheets<sup>65</sup> showed the superiority of a low-phosphorus, low-sulphur Bessemer steel over wrought iron.

When a protective coating of paint, tar, tin or zinc is applied, iron invariably shows better qualities than steel, but this is due to the fact that, on account of its rougher surface after cleaning, iron will take a heavier and more closely adherent coating than steel.

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A sheet made of very pure iron is superior to one of mild steel, as shown by the following tests:<sup>66</sup>

	Corrosion ratios.	
	Iron Sheet	Steel Sheet
Cold sulphuric acid (3.6%).....	100	1600
Air and moisture.....	100	280
Sulphur dioxide and moisture (cold).....	100	112
Sulphur dioxide-strong solution in water...	100	108

The chemical composition of these sheets was as follows:

	Iron Sheets	Steel Sheets
Carbon .....	0.018%	0.09 %
Manganese.....	0.024%	0.39 %
Phosphorous .....	0.040%	0.104%
Sulphur .....	0.023%	0.053%
Silicon .....	0.036%	.....

## INFLUENCE OF THE IMPURITIES IN THE METAL

All non-homogeneous metals and therefore all commercial irons and steels are doomed to decay unless adequately protected. Of the impurities in steel, the non-metals, with the exception of sulphur, seem to protect. In the case of metallic impurities, those which, like manganese, are themselves more liable to corrosion than the iron, will act unfavorably; others, like nickel and chromium, which are not so sensitive, will protect the iron with which they are alloyed, notwithstanding the fact that by mechanical contact they hasten the rusting; if unalloyed they act adversely, creating centers for pitting. Eutectic areas create centers for corrosion.

The nature and amount of the impurities in steel have a marked influence on its corrodibility. Carbon, inasmuch as it will allow hardening, will act as a protection, provided it is combined with the iron and uniformly distributed; high carbon steel is less corrodible than mild steel or iron. Black oxide only protects provided it is continuous and firmly "anchored" to the iron (Bower-Barffing, etc.); as mill-scale which is loose and fissured, it is detrimental, the iron in contact with it and exposed, rusts about 50% faster.

The gray cast-iron, in which combined carbon is

deficient, rusts more rapidly than other grades. Spiegeleisen<sup>67</sup> resists corrosion better than cast-iron because it is dense and high in carbon. Prof. Howe calls attention to the mechanical protection afforded by carbon as rusting proceeds, in the following words:<sup>68</sup> "As steel is gradually corroded away, more and more of its surface should come to be composed of cementite, and this fact should tend to retard the corrosion of steel, because cementite should protect the underlying free iron or ferrite." And elsewhere: "The cementite is in such extremely minute microscopic plates that the eating away of a very small quantity of the iron from above them ought to bring very nearly the full proportion of this cementite to the surface." It may be stated further that the definite compound, cementite, is much harder than iron—6.5 as against 4.5—and that it is soluble only in boiling hot acids.

Dr. W. L. Dudley found<sup>69</sup> that the presence of coal-gas in the ground materially retarded the corrosion of wrought iron pipe buried in it. In one test at Nashville, the presence of the gas reduced the rate of corrosion by one-half. It has also been found that gas-holders resist corrosion well on the inside, notwithstanding the water of condensation. Various methods of carbonating the surface of iron and steel are in use for protecting them against corrosion and are effective wherever there is little or no wear.

Graphite in iron, which is equivalent to uneven distribution of carbon, may promote rusting, but

graphite applied to the outside is conceded to be second to red-lead only as a protection for iron work (Archbutt); this protection is, no doubt, purely mechanical, although Dr. E. G. Acheson claims that steel, if immersed in water containing deflocculated graphite, does not rust as when the graphite is not added.

Sulphur accelerates corrosion. According to Moody,<sup>70</sup> sulphur compounds in iron and steel on exposure to air and water at once furnish free acid.

Phosphorus and silicon both appear to retard corrosion, and this effect may, as in the case of carbon, have some connection with their hardening qualities, or cold-shortening power. If, however, they are present in patches, like the oft-occurring phosphide eutectics, the softer parts, through contact action with the parts rich in phosphorus and silicon, will be destroyed all the more rapidly. Some authors have claimed that these two elements increase corrosion, but there is no evidence to support the contention apart from the case of uneven distribution, which will make any of the impurities rust promoters to a greater or lesser extent. The fact that common iron does not rust as rapidly as the better grades has been attributed by some to the greater percentage of phosphorus in the former. It might also be stated that charcoal-iron is free from manganese, and this might bear some relation to its qualities.

The alloys of silicon and iron which are known as "Metallures" show remarkable resistance both to

acid and atmospheric corrosion; this resistance increases with the percentage of silicon; above a content of 20% Si there is practically no action. Unfortunately, these alloys lack malleability, but apparatus made from them is used under such severe conditions as carrying and condensing hydrochloric acid.<sup>71</sup>

Dr. Dudley discovered, some years ago, that segregated manganese formed centers of corrosion, and it is a generally accepted fact that steels high in manganese are peculiarly liable to oxidation; if the proportion is small and uniformly distributed the effect is inconsiderable. The effect of manganese is corroborated by many reliable authorities.<sup>72</sup> The mixing of finely divided iron and manganese and subsequent exposure to oxidizing agents will result in rapid oxidation of both metals, the manganese itself being oxidized more rapidly than the iron; if placed in water the electrolytic action is evidenced by an appreciable and continuous disengagement of hydrogen. If pieces of iron and manganese are connected the latter will corrode and protect the iron (Walker). According to R. Dubois,<sup>73</sup> some ferro-manganese originally carrying 79.99 per cent of manganese was partially disintegrated by exposure to the weather. The powdery part held 82.17 per cent of manganese, and the mass had shrunk to one-half of its original bulk; this goes to prove the instability of the combination between the two metals. It has already been mentioned that manganese increases the occlusion of gases.

If the metals are alloyed the alloy is more electro-positive than the iron by itself and therefore more readily corroded. Up to a certain percentage manganese dissolved in iron will increase the electrical resistance of the metal, and the loss of conductivity may reach 50 per cent (Cushman). This fact is, no doubt, intimately connected with its corrodibility, the broad rule being that the better conductor a metal is the less it is liable to corrosion; the conductivity of a metal is always reduced by the addition of a less conducting metal; hydrogen is in the same class as the metals. It is known that manganese salts fix oxygen on certain compounds, and that even the solid salts at suitable temperatures hasten the oxidation of many substances; the metal itself will precipitate iron from its solutions, and it is reasonable to infer that with iron going into solution in the presence of oxygen, if there is any manganese present, it will aid its precipitation as an oxide. As silicon has the property of hardening manganese, a small percentage doing so to a considerable extent, the influence of manganese in promoting corrosion may be modified by that element.

The combination of manganese and sulphur shows a larger difference of potential to iron than manganese alone. The sulphur in steel will unite more readily with the manganese than with the iron, giving a gray sulphide. Some valuable investigations of the effect of manganese sulphide on the quality of rails have quite recently been carried

out by Dr. Henry Fay and J. E. Howard.<sup>74</sup> These investigators show that manganese sulphide separated in the form of fibers is a source of danger in steel rails, so that, apart from reasons relating to corrodibility, the combination of high manganese and high sulphur is to be avoided as a measure of safety.

The protection afforded by paints containing manganese dioxide ( $\text{MnO}_2$ ), even after their removal, seem to be due, not to the power which the salt possesses of decomposing hydrogen peroxide, but to the creation of a passive condition due to the formation of a film of black oxide (Wood); by using a very active oxidizing agent in a paint, it is claimed that slight inoxidation may be brought about and rusting inhibited; some tests of this theory made within recent years have not borne it out. If a Venetian-red ( $\text{Fe}_2\text{O}_3$ ) paint is used there cannot be any protection, even in theory—and almost anything can be done in theory—all metals are electro-positive to their own oxides, and on this account paints containing oxides of the metals to be painted are undesirable from a galvanic standpoint. An ideal method for protecting steel against corrosion would consist in giving it a perfectly homogeneous surface before painting, either by removing slag, manganese, sulphur and other impurities chemically, or by depositing electrolytic iron upon it, using a depolarizer to take care of the free hydrogen.

## COMPARATIVE CORROSION OF ACID AND BASIC STEELS.

Alexander G. Fraser, in a paper read before the West of Scotland Iron and Steel Institute in 1907,<sup>75</sup> gave the results of an extensive investigation of the relative corrodibility of acid and basic steels.

Excepting in the sulphuric acid test, the acid steel was a trifle less attacked than the basic; this may have been due to the manganese being higher in the basic steel, although the phosphorus was lower. In the case of the sulphuric acid test (sp. gr. 1.05) the basic steel resisted far better than did the acid steel to the extent of from 8.43 to 26.24%; the skin of the basic steel plates was scarcely attacked, whereas most of the acid plates were badly corroded. Mr. Fraser suggested that this might have been due to the carbon being in a different condition in the two steels and a sort of case-hardening of the surface of the basic plates having taken place during rolling; this would vitiate judgment as applied to the body of the metals. From the figures given in the table it would appear that the popular notion about the excessive corrodibility of basic steel is unfounded.

## INFLUENCE OF THE ELECTRIC CURRENT.

Interesting tests of the effect of an electric current on the speed of corrosion of a steel plate were made by Mr. Gardner, of the Scientific Section of the American Paint Manufacturers' Association;<sup>76</sup> the results of the normal tests without current under different conditions are worth comparing with those of earlier experimenters, but the increase in the rate, due to the passage of a current of  $1\frac{1}{2}$  volt, is specially worthy of attention. The following is a summary of the results:

1.	Distilled water boiled.....	0.0482
1A.	Same with electric current.....	0.0870
2.	Distilled water and oxygen.....	0.0601
2A.	Same with electric current.....	0.1211
3.	Distilled water and ozone.....	0.0768
3A.	Same with electric current.....	0.1155
4.	Pure air, oxygen and nitrogen.....	0.0492
4A.	Same with electric current.....	0.0911
5.	Pure air, with ammonia; oxygen, nitrogen and ammonia. (Little oxide precipitated. Color dark.)	0.0406
5A.	Same with electric current..... (Little oxide precipitated. Color dark.)	0.0758
6.	Pure air with ammonia; oxygen, nitrogen and carbonic acid..... (Color of oxide brighter than any of foregoing.)	0.1030
6A.	Same with electric current..... (Color of oxide brighter than any of foregoing.)	0.1941
7.	Pure air with ammonia and carbonic acid..... (Color of oxide brighter than any of foregoing.)	0.0921
7A.	Same with electric current..... (Color of oxide brighter than any of foregoing.)	0.1876

In each case the action seems to have been about doubled in its intensity by the passage of the current.

Alternating currents have less effect on the corrosion of iron than direct currents (Gee).

## IRON AND STEEL EMBEDDED IN CONCRETE

Reinforced concrete is undoubtedly the building material of the future, because of the wide distribution of cement material and also because this combination of concrete and steel has proved itself within the last few years the best for every purpose and from all points of view except, possibly, that of beauty of form. The one and only serious objection which has been raised against it is the permanence of the reinforcement; it is a question of paramount interest.

In reinforced concrete construction the steel reinforcement gives the material the requisite quality for undergoing flexional strains under which concrete by itself would fail, as would natural stone, notwithstanding its high resistance to crushing. To take advantage of its qualities, the reinforcement must be placed below the concrete, although additional reinforcement may be required on the upper part to take care of negative bending moments. The mortar which is applied to the other side of the reinforcement—the lower side in the case of floors and beams—must be sufficient to protect it against fire and corrosion. The lighter coating is usually  $1\frac{1}{2}$  inch or more in thickness, depending on its composition, and therefore its ability to resist

the disintegrating effect of fire applied for a long time; its composition should be such as to afford full protection against corrosion. It is remarkable but true that but little attention is paid to the latter consideration, although it is fully as important as the protection against fire.

The majority of tests which have been undertaken to secure data on the corrodibility of steel in concrete have resulted in the broad conclusion that when properly mixed and applied, Portland cement concrete is an ideal protection against rusting. There is a well-known case of iron hoops embedded in cement for 26 years, which were found unimpaired and with the blue mill-scale intact.<sup>77</sup> Whether or not, as claimed by Breuillé, cement removes any rust which may have existed on the metal when it was embedded is of secondary importance compared to the action it may have on the unimpaired metal.

Neat *Portland* cement is known to be an excellent protection against rusting; it has been successfully used as paint for the protection of large structures, notwithstanding its lack of flexibility. On account of this quality it is well to endeavor, wherever possible, to fill in and around the reinforcement and in immediate contact with its surface with a concrete high in cement and holding a smaller percentage of small gravel or broken stone than what is to be laid above it; it should also be applied very wet to insure good contact and the formation of a film of neat cement on the surface

of the reinforcement; for the protective coating a rich mortar, as wet as can be used, is advisable.

Prof. S. B. Newberry has explained as follows the protective action of Portland cement: "Portland cement contains about 63 per cent lime. By the action of water it is converted into a crystalline mass of hydrated calcium silicate and calcium hydrate. In hardening it rapidly absorbs carbonic acid and becomes coated on the surface with a film of carbonate, cement mortar thus acting as an efficient protector of iron, and captures and imprisons every carbonic-acid molecule that threatens to attack the metal. The action is, therefore, not due to the exclusion of the air, and even though the concrete be porous, and not in contact with the metal at all points, it will still filter and neutralize the acid and prevent its corrosive effect." This explanation will no doubt satisfy the followers of the carbonic-acid theory of corrosion, but the fact will remain that at points where there is no contact between the cement and the metal corrosion does quite often take place; however, the protection against carbonic acid afforded by the cement must be an efficient retarder of corrosion. An insoluble carbonate is an excellent impermeable screen against corrosive influences, and its value is well illustrated by the remarkable passivity of sheet-zinc roofing which has been weathering for scores of years on thousands of buildings in European cities.

With many styles of reinforcement, it is difficult to employ a selected strength of mix in immediate

contact with the steel; with reinforcements made from sheet metal it can, as a rule, be readily done. Plain rods would seem to be the best to use, deformed ones being liable to cause air-pockets. Prof. Chas. L. Norton has made tests which show that while neat cement affords perfect protection to steel, concrete does not; it is thus of the very greatest importance that the cement be sufficiently wet to insure a film of neat cement forming on the surface of the reinforcement, and that the concrete be everywhere well rammed.

As far as subsequent rusting is concerned, it would seem to be of little importance whether the reinforcement be clean and free from rust or not at the time of embedding, provided the concrete lie close to it and form an impermeable skin over it; it is, however, an important consideration to secure proper adhesion of the steel to the cement. Especially is this necessary in the case of wire, which must not draw through the cement in case an anchorage fails or it is rusted through at one point. Galvanizing or painting the reinforcement is a pure waste of money, and both are liable to introduce agents of corrosion, such as chlorides, metallic oxides and organic acids; they furthermore prevent the proper adhesion of the cement. A dip of tar asphaltum would perhaps be beneficial; the best practice is, perhaps, to dip the reinforcement in a neat cement grout before using it.<sup>78</sup>

Cinder concrete is more porous than that which contains a stone filler, and opposes less resistance

to shear, and for these reasons it is less desirable in reinforced work; it is still a matter of some doubt if the small amounts of sulphur and iron oxide which are present in the cinder can have any effect worth considering on the reinforcement; it is, however, not advisable to use it around the reinforcement, especially where, as in the case of wire, "splitting" is to be avoided. For similar reasons it is best not to use slag cement until it has been definitely proved that steel is no more liable to rust in it than in genuine Portland concrete.

According to Breuillé, if water is allowed to pass through the concrete the neat cement film in contact with the steel will disappear and rusting will take place; it is thus advisable to waterproof exposed surfaces—as is always done in the case of roofing—or to use an opaque reinforcement such as specially crimped or corrugated sheets; even then the water, if it cannot go through, will work its way out laterally. If acids or other corrosive liquids can reach the reinforcement, special surface protection of the concrete is imperative.

Cement has been used for the inside of ships to protect the hull against the internal corroding agencies which are the most severe. Barges, pontoons, floating stages and even row-boats have been built entirely of reinforced concrete. This system was first used for boats and pontoons by Lambot-Miraval, a Frenchman, in 1850.

There is a great deal of literature published on the subject of reinforced concrete, and the conclu-

sions to be derived from it are that it is safe to use modern rustable steel reinforcement, provided it is clean, and a coating of neat Portland cement on its surface is insured by using a rich and wet mix with clean sand and trap rock, limestone or other hard and passive filler, in immediate contact with it, and avoiding voids by careful tamping. The fact that concrete structures are monolithic and become stronger with age and also because the factors of safety allowed are—and should remain—conservative, we are justified in feeling convinced of their permanence, even if through carelessness during erection the reinforcements suffer a partial decay. It would be unwise, however, not to provide against such decay and to allow it to go to the length of total destruction.

## THE INHIBITION OF RUSTING

By the inhibition of rusting is meant its restriction or repression, not its complete prohibition; inhibition means an extension of life for the iron; the protective effect is, sooner or later, overcome and clearly indicates that inhibition furnishes something to the iron, be it substance or physical state, which, under the attacks of corrosive agencies, is slowly expended until destroyed or brought below the safe limit of protection.

Inhibitory treatments have the effect of rendering the iron or steel passive. Passivity to chemical action may have a mechanical or electrical cause. In some cases it seems to be due to the formation of a neutral screen between the corroding agents and the iron; in other cases it seems to be due to a zone of occluded matter or gas which affords galvanic protection. This last is apparently the nature of the protection afforded iron which has undergone any of the inhibitory treatments which have so far been tried.

The fact, pointed out by Dr. Cushman, that treated iron will take on an adherent coating of copper from a sulphate solution in less than one-sixth the time required when it is untreated, is

sufficient proof that the electrolytic action which causes the precipitation of the copper has been intensified by the inhibitory treatment; the difference of e.m.f. between the copper ions and the iron is greater. The investigator points out further that the protective effect can evidently not be due to a film of oxide.<sup>79</sup>

That strong oxidizing agents would render iron passive has been known for a long time. Prof. Bloxam in 1868<sup>80</sup> showed that iron which had been dipped in pure nitric acid for a length of time was not affected by the same acid dilute. The fuming sulphuric acid will have a similar effect. Arsenic and its derivatives likewise inhibit rusting.<sup>81</sup> Moody mentions also sodium nitrite and potassium ferrocyanide.

The best way to examine the subject of inhibition is to take advantage of the work of Dr. Cushman and analyze the following facts, expressed in his own words:

1. "All substances which develop hydroxyl ions in solution, such as the alkalis or salts of strong bases with weak acids, to a certain extent inhibit, and, if the concentration is high enough, absolutely prohibit the rusting of iron."

2. "No rusting occurred in any solutions of or above a strength corresponding to about 8 parts of potassium bichromate in 100,000 parts of water, or about 2 pounds to 3,000 gallons."

In both of these cases the objects treated were kept in the treating solutions. Potassium bichro-

mate and chromic acid appear to be of benefit for retarding the inception of rusting, under proper conditions of concentration and condition of the surfaces treated.

3. "No visible change is effected, for the polished surfaces examined under the microscope appear to be untouched. If, however, the polished strips are immersed in water, it will be found that rusting is inhibited for a matter of hours, days or even weeks."

The impossibility of detecting any change tends to show that no chemical alteration of the surface has taken place; the final overcoming of the protection by corroding agencies shows that the attacks of those agencies exhaust the power accumulated by the treatment, and that, therefore, some kind of destructive effect on whatever was left in the iron by the treatment is taking place, until finally the metal loses its immunity and is corroded in the ordinary way.

Moody explains the action of chromic acid as due to the removal of constituents which would yield acids on exposure to water and oxygen. He claims that iron is dissolved in chromic acid and that chromated iron is oxidized in normal air containing  $\text{CO}_2$ . Actual experiments with properly chromated steel does not confirm its corrodibility in normal air.

4. "If a polished surface, which has been rendered passive by immersion in bichromate, is heated to  $100^\circ \text{C}$ . for some hours, its passivity dis-

appears and it again behaves in a normal mannner."

5. "A chromated strip of iron which is kept in a vacuum soon loses its passivity, whereas a similar strip kept under ordinary conditions remains passive for long periods."

These last two facts are strongly suggestive of the presence of an occluded gas, which can be baked out or diffused out in a vacuum.

6. "The phenomenon of passivity is produced only by strong oxidizing agents or by galvanic contact when oxygen can separate on the iron."

As we have seen, when iron is anode and dissolves it will rust, and hydrogen, which is negative to it, will be precipitated. In the present case we have the condition of oxygen being precipitated, showing that the iron is cathode. In the case of rusting we had free dissociated hydrogen, inducing corrosion by its contact effect on the iron, now we have free dissociated oxygen inhibiting rusting by what we may well be allowed to surmise is likewise a contact effect. Hydrogen, which in itself is suggestive of reduction, is the *indicator* of the opposite reaction of oxidation, and oxygen, which suggests oxidation, is the indicator of reduction. This fact is very well illustrated in the process of pickling by electricity,<sup>82</sup> in which the metal to be pickled is put in a weak acid solution and connected as cathode in a circuit of low voltage, whereby the scale is rapidly reduced.

7. "According to Mugdan,<sup>83</sup> the passivity is due to lowering of the potential of the metal."

8. "If polished iron is allowed to stand for some time in standard tenth-normal potassium bichromate solution, the oxidizing strength of the latter, as measured by its titration value, is slightly reduced without the solution of the iron or the production of any visible effect."

This bears out the argument that oxygen is absorbed by the metal and that, being positive to iron, its contact effect is to render the iron immune as cathode so that it will not dissolve; the positive partner of the couple thus formed is the object of the attacks of the agencies which cause the rusting of iron. As we have seen, hydrogen in a free condition is "the enemy"; the inhibitory effect is therefore destroyed by the union of the attacking hydrogen ions to the oxygen in the surface of the treated iron. When hydrogen has combined with all the oxygen the iron has lost its passivity and rusting proceeds.

9. "In order to show beyond doubt that an oxygen electrode is formed by immersing iron in a strong solution of bichromate, the following experiment was made: Two polished steel electrodes were prepared and chromated by immersion for a number of hours in a strong solution of potassium bichromate. The prepared electrodes were then thrust tightly through a rubber stopper which closed a flask which was then filled with pure freshly boiled distilled water. The electrodes were then attached to the poles of a primary battery of about 2 volts potential. At the end of half an

hour, although the potential was not sufficient to disengage bubbles of gas and no visible change had occurred, the electrode which was connected to the zinc pole of the battery had lost its passivity, the other retaining it."

Rapid depolarization had thus been effected by a reversal of current; under ordinary circumstances slow depolarization, which finally does away with the benefits of the treatment, is brought about by natural agencies.

Cushman's conclusions are that from the evidence, the passivity of iron is best explained as a polarization effect produced by the separation and retention of oxygen on the surface of the metal and that the protection afforded by certain oxidizing agents is electro-chemical and not mechanical; that if the rusting of iron is due primarily to the action of hydrogen ions, iron in the condition of an oxygen electrode should be more or less well protected from electrolytic attack.

The corrosion of other metals may likewise be inhibited by treatment with the bichromates of sodium and potassium, and the author has found that galvanized work treated in this manner would retain its color and be improved in quality.

Inhibitory treatments are valuable for application in connection with various shop processes, but they offer no permanent solution to the problem of protecting iron and steel against corrosion. The improvement of the quality of the metals themselves and proper treatment of their surface, both

mechanically or by the incorporation of other metals previous to coating with paints or malleable metal deposits, would seem to constitute the most promising field for research.

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- <sup>80</sup> *Proc. Soc. C. E.*, Yr. 1868, p. 567.
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## GENERAL BIBLIOGRAPHY.

The following is a selection of the more important articles on the Corrosion of Iron and Steel, taken from the very valuable and complete Bibliography of Metal Corrosion and Protection published by the Carnegie Library of Pittsburgh.\*

The following abbreviations have been used:

Diag.	diagrams.	p.	page.
Dr.	drawings.	pl.	plate.
Ill.	illustrations.	v.	volume.
n. d.	no date.	w.	words.
n. s.	new series.		

## GENERAL.

**Adie, R.**

On the corrosion of metals. 10 p. 1845. (In Minutes of Proceedings of the Institution of Civil Engineers, v. 4, p. 323.)

Shows that saturated salt solutions are a great protection from corrosion.

**Akerman, R.**

Ueber das rosten des eisens. 4,200 w. 1882. (In Stahl und Eisen, v. 2, p. 417.)

Considers theory of rusting, especially of protective metal coatings, and of the influence of manganese in the rusting of steel.

**Alford, H. Carroll.**

Corrosion of iron and its prevention. 2,200 w. 1901. (In Proceedings of the St. Louis Railway Club, v. 5, April 12, p. 9.)

Theory of rust formation and preventive measures.

**American Society for Testing Materials.** 1,800 w. 1906. (In Iron Age, v. 77, p. 2057.)

Abstracts of papers at ninth annual meeting of the society; corrosion of tube steel, corrosion of wire fencing, electrolysis in structural steel, etc.

**Andes, Louis Edgar.**

Der eisenrost; seine bildung, gefahren und ver-hütung unter besonderer berücksichtigung der ver-wendung des eisens als bau- und constructionsmaterial. 292 p. Ill. 1898.

Treats very fully of rust formation and gives many methods of prevention, chiefly by preservative paints.

\* 57 pp., price 10 cts., postpaid.

**Calvert, F. Crace.**

Experiments on the oxidation of iron. 1,000 w. 1871. (In Chemical News, v. 23, p. 98.)

Paper before the Manchester Literary and Philosophical Society.

Indicates that "carbonic acid is the agent which determines the oxidation of iron."

**Corrosion** of iron. 4,700 w. 1907. (In Electrochemical and Metallurgical Industry, v. 5, p. 363.)

Gives in condensed form papers by Walker and Cushman.

See also editorial, p. 343.

**Cranfield, W.**

Iron; its oxidation, corrosion, protection. 7,000 w. 1909. (In Journal of Gas Lighting, v. 106, p. 443.)

Paper before the Yorkshire Junior Gas Association.

Discusses theory, corrosive agents and the preservative values of various coatings.

**Crowe, Edward.**

Corrosion of iron and steel. 2,600 w. Dr. 1909. (In Proceedings of the Cleveland Institution of Engineers, session of 1908-09, p. 148.)

*The same, condensed.* 1,200 w. (In Iron and Coal Trades Review, v. 78, p. 341.)

Discussion.

Does not enter into the theory of corrosion, but describes special instances and suggests causes and methods of prevention.

**Cushman, Allerton, S.**

Corrosion of iron. 35 p. Dr. ill. 1907. (In United States—Office of Public Roads. Bulletin No. 30.)

*The same.* (In Chemical News, v. 99, p. 8, 14.)

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See also editorial, p. 995.

*The same, condensed.* 5,500 w. (In Scientific American Supplement, v. 64, p. 151.)

Abundant references to original sources.

Describes and illustrates experiments of the author tending to establish the electrolytic theory of corrosion. Author's own belief is that "the whole subject . . . is an electrochemical one, which can be readily explained under the modern theory of solutions."

Corrosion of iron. 18 p. Dr. ill. 1907. (In Proceedings of the American Society for Testing Materials, v. 7, p. 211.)

Corrosion of steel. 4,000 w. 1908. (In Journal of the Franklin Institute, v. 165, p. 111.)

Preservation of iron and steel. 11,000 w. Ill. 1909. (In Iron and Coal Trades Review, v. 78, p. 735.)

*The same.* (In Engineering, v. 87, p. 710, 742.)

*The same, slightly condensed.* (In Engineer, London, v. 107, p. 537, 565.)

*The same, slightly condensed.* (In Ironmonger, v. 127, p. 14.)

Paper before the Iron and Steel Institute.

Consideration of the nature and degree of protection to metals by metallic coatings, paints and cement, with applications of the electrochemical theory.

**Friend, J. Newton.**

Rusting of iron. 28 p. Dr. 1908. (In Journal of the Iron and Steel Institute, v. 77, p. 5.)

Experimental results indicate that "the rusting of iron is primarily the result of acid attack" rather than of electrochemical nature and that the hygroscopic nature of rust underlies its corrosive action.

**Gee, W. W. Haldane.**

Electrolytic corrosion. 6,500 w. Diag. dr. 1908. (In Electrician, London, v. 61, pp. 66, 98.)

*The same, condensed.* 4,500 w. (In Electrical Engineering, London, v. 3, p. 559.)

*The same, condensed.* 1,300 w. (In Electrical Review, London, v. 62, p. 692.)

Paper before the Manchester local section of the Institution of Electrical Engineers.

Notes on conditions under which corrosion takes place.

**Hambuechen, Carl.**

Experimental study of the corrosion of iron under different conditions. 40 p. Diag. ill. 1900. (In Bulletin of the University of Wisconsin; engineering series, v. 2, no. 8.)

"Bibliography," p. 274.

Concludes that character and rapidity of corrosion depend upon physical and chemical properties of the object and that "the application of stress to metals causes an increase in chemical activity."

**Heyn, E. & Bauer, O.**

Ueber den angriff des eisens durch wasser und wässrige lösungen. 104 p. Folding pl. 1908. (In Mitteilungen aus dem Königlichen Materialprüfungsamt, v. 26, p. 1.)

*The same, condensed.* 4,800 w. (In Stahl und Eisen, v. 28, p. 1564.)

*The same, abstract translation.* 400 w. (In Journal of the Iron and Steel Institute, v. 78, p. 663.)

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**Howe, Henry M.**

Corrosion of iron. 11 p. 1895. (In his *Metallurgy of Steel*, ed. 4, v. 1, p. 94.)

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**Lindsay, Charles C.**

On the corrosion and preservation of iron and steel. 32 p. Dr. 1881. (In *Transactions of the Institution of Engineers and Shipbuilders in Scotland*, v. 24, p. 77.)

*The same, condensed.* 2,000 w. (In *Scientific American Supplement*, v. 12, p. 4570.)

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Experiments on the relative rates of corrosion of different irons in fresh and salt water and the protection of iron and steel by coatings of paint or metal.

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**Mugdan, M.**

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*The same, abstract.* 250 w. (In *Journal of the Iron and Steel Institute*, v. 64, p. 720.)

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**Newman, John.**

Metallic structures; corrosion and fouling and their prevention; a practical aid-book to the safety of works in iron and steel, and of ships, and to the selection of paints for them. 374 p. 1896.

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**Thurston, Robert H.**

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**Davis, R. O. E.**

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**Dunstan, Wyndham Rowland, and others.**

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Considers influence of kind of substance on chemical corrosion, influence of temperature on corrosion and includes table showing corrosion series of the metals at 60° F. and 160° F.

Some relations of heat to voltaic and thermo-electric action of metals in electrolytes. 2,800 w. 1883. (In *Proceedings of the Royal Society of London*, v. 36, p. 50.)

Abstract. Many experiments tended to show that "the most chemically-positive metals were usually the most quickly corroded, and the corrosion . . . was usually the fastest with the most acid solutions. . . . Corrosion was not the cause of pure thermo-electric action of metals in liquids.

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Lecture before the Institute of Marine Engineers.

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Rusting of iron. 3,300 w. Dr. 1906. (In *Journal of the Chemical Society*, v. 89, pt. 1, p. 720.)

Challenges Dunstan's conclusions and asserts that carbonic acid must be present, in however minute quantity, before rusting begins.

**Pennock**, J. D. & **Morton**, D. A.

Commercial aqua ammonia; its effect upon iron, its impurities, and methods for determining them. 3,500 w. 1902. (In *Journal of the American Chemical Society*, v. 24, p. 377.)

Concludes that concentrated ammonia solutions not only do not rust clean iron, but prevent its rusting in the presence of corrosive agents.

**Richards**, Theodore William, & **Behr**, G. E., Jr.

Electromotive force of iron under varying conditions, and the effect of occluded hydrogen. 43 p. Diag. dr. 1906.

Takes issue (p. 20) with conclusion that corrosion is necessarily increased by stress.

**Rusting** of iron. 1906-07. (In *Nature*, v. 74, p. 540, 564, 586, 610; v. 75, p. 31, 390, 438, 461.)

Letters by Friend, Moody, Richardson, Meehan, Dunstan and Stromeyer concerning the theory of rusting and the action of carbon dioxide.

**Schleicher**, A. & **Schultz**, G.

Untersuchungen über das rosten von eisen. 2,400 w. Diag. 1908. (In *Stahl und Eisen*, v. 28, p. 50.)

Experiments on the differences of potential of metal plates separated from one another in water.

**Tilden**, William Augustus.

Rusting of iron. 3,500 w. Dr. 1908. (In *Journal of the Chemical Society*, v. 93, p. 1356.)

Shows that carbonic acid is not necessary to corrosion, but that it hastens the action and that rusting is due initially to electrolytic action, resulting in the production of ferrous hydroxide or carbonate.

**Traube, Moritz.**

Ueber die mitwirkung des wassers bei der langsamen verbrennung des zinks, bleis, eisens und palladiumwasserstoffs. 3,400 w. 1885. (In Berichte der Deutschen Chemischen Gesellschaft, v. 18, pt. 2, p. 1877.)

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**Walker, William H. and others.**

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*The same.* (In Chemical News, v. 97, p. 31, 40.)

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Paper before the Iron and Steel Institute.

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*The same, condensed.* 1,700 w. (In Electrochemical and Metallurgical Industry, v. 7, p. 150.)

Considers the corrosion of zinc-plated iron wire and of tubes and shells of steam-boilers.

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**Walker, William H. & Dill, Colby.**

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*The same, condensed.* 1,800 w. (In Electrochemical and Metallurgical Industry, v. 5, p. 270.)

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Experimental results tend to show that differences of potential are not necessarily the result of stress.

Influence of stress upon the corrosion of iron. 3,100 w. **Diag.** 1907. (In Proceedings of the American Society for Testing Materials, v. 7, p. 229.)  
Discussion, 500 w.

**Whitney, W. R.**

Corrosion of iron. 5,000 w. **Dr.** 1903. (In Journal of the American Chemical Society, v. 25, pt. 1, p. 394.)

Emphasizes fact that the effect of carbonic acid on corrosion is cyclic and that under favoring conditions "even a trace of carbonic acid may dissolve an unlimited quantity of iron."

### EFFECT OF IMPURITIES.

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Ueber den einfluss der reihenfolge von zusätzen zum flusseisen auf die widerstandsfähigkeit gegen verdünnte schwefelsäure. 1,000 w. **Diag. dr.** 1905. (In Mitteilungen aus dem Königlichen Materialprüfungsamt, v. 23, p. 292.)

Considers the influence of aluminium and tungsten on the corrosion of steel in dilute sulphuric acid.

**Breuil, Pierre.**

Corrosion tests on copper steels. 400 w. **Dr.** 1907. (In Journal of the Iron and Steel Institute, v. 74, p. 41.)

Experiments using sulphuric acid as corrosive liquid "make copper steels rank in value with nickel steels in respect of corrosion."

Corrosion tests on the [copper] steels as rolled. 1,200 w. 1907. (In Journal of the Iron and Steel Institute, v. 74, p. 60.)

Tests show corrosion to take place much more slowly with rolled steel.

**Huntly, G. Nevill.**

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Considers action resulting from the solution of the sulphur present as sulphid in the boiler metal.

**Williams, F. H.**

Influence of copper in retarding corrosion of soft steel and wrought iron. 400 w. 1900. (In Proceedings of the Engineers' Society of Western Pennsylvania, v. 16, p. 231.)

Indicates that presence of copper retards corrosion.

**Yarrow, A. F.**

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**Discussion.**

From experimental results assumes that both from acid corrosion and from the action of steam nickel steel boiler-tubes will be far more durable than those of mild steel.

ACID TESTS.

**Burgess, Charles F. & Engle, S. G.**

Observations on the corrosion of iron by acids. 3,000 w. 1906. (In Transactions of the American Electrochemical Society, v. 9, p. 199.)

Effect of normal solutions of sulphuric and hydrochloric acids on electrolytic iron.

**Report** of committee U on the corrosion of iron and steel. 700 w. 1907. (In Proceedings of the American Society for Testing Materials, v. 7, p. 209.)

Offers suggestions as to the conditions for experiments on the connection between the rapidity of solution in acid and natural corrosion.

**Report** of committee U on the corrosion of iron and steel. 2,000 w. Diag. 1908. (In Proceedings of the American Society for Testing Materials, v. 8, p. 231.)

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RELATIVE CORROSIONS.

**Fraser, Alexander G.**

Relative rates of corrosion of acid and basic steel. 16 p. Folding pl. 1907. (In Journal of the West of Scotland Iron and Steel Institute, v. 14, p. 82.)

**Discussion,** p. 112. 20 p.

*The same, condensed.* 1,600 w. (In Iron Age, v. 79, p. 1196.)

Tests in air, river water, salt water and sulphuric acid.

**Howe, Henry M.**

Relative corrosion of wrought iron and steel. 5,600 w. 1895. (In Mineral Industry, v. 4, p. 429.)

*The same, condensed.* 1,600 w. (In Journal of the Iron and Steel Institute, v. 50, p. 427.)

Gives results both from laboratory experiments and from actual industrial use.

Relative corrosion of wrought iron, soft steel and nickel steel. 1,500 w. Dr. 1900. (In Engineering and Mining Journal, v. 70, p. 188.)

Relative corrosion of wrought iron and steel. 1,800 w. Dr. 1906. (In Proceedings of the American Society for Testing Materials, v. 6, p. 155.)

**Discussion,** 7,000 w.

*The same, condensed.* 1,300 w. (In *American Machinist*, v. 29, p. 49.)

*The same, condensed.* (In *Engineering Magazine*, v. 31, p. 750.)

*The same, condensed.* (In *Industrial World*, v. 40, p. 228.)

*The same, condensed.* (In *Iron Age*, v. 77, p. 2047.)

Rapid corrosion of steel in many instances may be due to the inferior quality of the steel.

**Gruner.**

Recherches sur l'oxydabilité relative des fontes, des aciers et des fers doux. 1,000 w. 1883. (In *Comptes rendus des Séances de l'Académie des Sciences*, v. 96, p. 195.)

**Kosmann, B.**

Ueber die corrosion von fluss- und schweiseseisen und über den zerfall von legirungen. 2,100 w. 1893. (In *Stahl und Eisen*, v. 13, pt. 1, p. 149.)

*The same, condensed.* (In *Journal of the Iron and Steel Institute*, v. 43, p. 399.)

Difference in resistance to corrosion of ingot and weld is held to be due entirely to difference in their chemical composition.

**Parker, William.**

On the relative corrosion of iron and steel. 11,200 w. Dr. 1881. (In *Journal of the Iron and Steel Institute*, v. 18, p. 39.)

Effects of exposure in air, in sea-water, in marine boilers, etc.

**Pillips, David.**

On the comparative endurance of iron and mild steel when exposed to corrosive influences. 25 p. Dr. 1881. (In *Minutes of Proceedings of the Institution of Civil Engineers*, v. 65, p. 73.)

Discussion, 40 p.

Considers admiralty tests and tests by the author indicating greater resistance to corrosion of iron.

**Rudeloff, M.**

Bericht über vergleichende untersuchungen von schweiseseisen und flusseisen auf widerstand gegen rosten. 125 p. Ill. 1902. (In *Mittheilungen aus den Königlichen Technischen Versuchsanstalten*, v. 20, p. 83.)

*The same, condensed.* 4,000 w. (In *Stahl und Eisen*, v. 23, p. 384.)

*The same, abstract.* 1,500 w. (In *Journal of the Iron and Steel Institute*, v. 63, p. 713.)

Extensive experiments on the relative resistance to corrosion of wrought-iron and steel, considering the effect of different condi-

tions and coatings and giving the relative corrosive action of various agencies.

**Speller, Frank N.**

Puddled iron versus soft steel. 2,200 w. Ill. 1905. (In *Iron Age*, v. 75, p. 1666. 1881.)

Claims equal resistance of iron and steel to corrosion, in reply to statements of Roe.

Corrosion of iron and steel. 900 w. 1907. (In *Proceedings of the Engineers' Society of Western Pennsylvania*, v. 22, p. 472.)

*The same.* (In *Iron Age*, v. 79, p. 478.)

Discussion, 1,800 w.

Gives results of tests showing steel to be superior to wrought-iron.

### CORROSION IN SEA-WATER.

**Andrews, Thomas.**

On galvanic action between wrought-iron, cast metals and various steels during long exposure in sea-water. 5,000 w. Ill. 1884. (In *Minutes of Proceedings of the Institution of Civil Engineers*, v. 77, p. 323.)

Corrosion of metals during long exposure in sea-water. 7,500 w. Ill. 1885. (In *Minutes of Proceedings of the Institution of Civil Engineers*, v. 82, p. 281.)

**Diegel, H.**

Einiges über die korrosion der metalle im seewasser. 95 p. Folding pl. 1903. (In *Verhandlungen des Vereins zur Beförderung des Gewerbflusses*, v. 82, p. 91.)

*The same, condensed.* 4,500 w. (In *Zeitschrift des Vereines Deutscher Ingenieure*, v. 47, p. 1122.)

*The same, abstract.* 400 w. (In *Journal of the Iron and Steel Institute*, v. 65, p. 677.)

Extensive experiments lead author to claim that impure metals do not corrode in salt water faster than pure metals. Foreign elements introduced were phosphorus and nickel.

**Farquharson, J.**

Corrosive effects of steel on iron in salt water. 4,800 w. 1882. (In *Transactions of the Institution of Naval Architects*, v. 23, p. 143.)

Experiments indicating that contact of iron and steel should be avoided.

Discussion.

**Johnstone, George.**

Notes on the serious deterioration of steel vessels from the effects of corrosion. 7 p. 1901. (In *Trans-*

actions of the Institution of Engineers and Shipbuilders in Scotland, v. 45, p. 71.)

Discussion, 28 p.

Especially on corrosion of internal parts of vessels and on vessels in the tropics.

### **Lidy.**

Note sur l'altération des métaux par l'eau de mer. 2,200 w. Ill. 1897. (In Annales des ponts et chaussées, mémoires, ser. 7, v. 14, 3e trimestre, p. 338.)

*The same, condensed.* 900 w. (In Engineering News, v. 39, p. 85.)

Describes condition of metals after exposure to the action of sea-water for several hundred years.

### **Mallet, Robert.**

On the corrosion and fouling of iron ships. 60 p. 1872. (In Transactions of the Institution of Naval Architects, v. 13, p. 90.)

Discussion, 10 p.

"Catalogue of British patent inventions," p. 135, 17 p.

### **Sabin, Alvah Horton.**

Experiments on the protection of steel and aluminium exposed to sea water. 8,000 w. 1896. (In Transactions of the American Society of Civil Engineers, v. 36, p. 483.)

Condition of plates with various preservative coatings after six months' immersion in sea-water.

Discussion and correspondence.

Experiments on the protection of steel and aluminium exposed to water. 5,000 w. 1899. (In Transactions of the American Society of Civil Engineers, v. 43, p. 444.)

Continuation of above experiments.

Discussion.

*The same, condensed.* (In Engineering News, v. 40, p. 54.)

## **PIPES.**

**Committee** report on relative corrosion of wrought iron and steel pipes. 1,600 w. Dr. ill. 1909. (In Plumbers' Trade Journal, v. 14, p. 214.)

*The same, slightly condensed.* 1,300 w. (In Heating and Ventilating Magazine, v. 6, p. 12.)

Report to American Society of Heating and Ventilating Engineers.

Tests indicate steel pipe of good quality to be as durable as wrought-iron pipe.

**Corrosion** of pipe in coal mines. 450 w. Ill. 1906. (In Iron Age, v. 78, p. 80.)

Results showing superiority of "Spellerized" steel pipes in the sulphur water of coal mines.

**Dudley, William L.**

Effect of coal gas on the corrosion of wrought iron pipe buried in the earth. 1,100 w. 1908. (In Journal of the American Chemical Society, v. 30, p. 247.)

Experiments in earth saturated with coal gas, indicating that amount of corrosion is determined by the chlorine content in the earth.

**Howe, Freeland, jr.**

Action of water on pipes. 5,000 w. 1908. (In Journal of the New England Water Works Association, v. 22, p. 43.)

Consideration of the nature of water and of iron pipe and of the electrolytic action that takes place.

**Howe, Henry M. & Stoughton, Bradley.**

Relative corrosion of steel and wrought iron tubing. 20 p. Ill. 1908. (In Proceedings of the American Society for Testing Materials, v. 8, p. 247.)

Discussion, 15 p.

*The same.* (In Industrial World, v. 83, p. 1244.)

Believes that modern steel tubing is equal to wrought-iron tubing and that the prejudice against it is due to practical experience with older tubing.

**Knudson, Adolphus A.**

Electrolytic corrosion of the bottom of oil tanks and of other structures. 4,300 w. Dr. ill. 1908. (In Transactions of the American Electrochemical Society, v. 14, p. 189.)

Discussion, 900 w.

Corrosion of oil-tanks thought to be caused by galvanic action set up by the distribution of acid or alkaline electrolytes over the iron surface.

**McAlpine, William J.**

Corrosion of iron. 1,200 w. 1868. (In Transactions of the American Society of Civil Engineers, v. 1, p. 23.)

Cites instances of preservation of water-pipes, iron submerged in salt water, etc.

**Mason, William P.**

Action of water upon metals: tanks, pipes, conduits, boilers, etc. 19 p. Dr. 1902. (In his Water Supply, p. 394.)

Data compiled from various sources, giving references.

**Rust** in galvanized iron water service pipe. 6,000 w. 1909. (In Metal Worker, v. 71, March 27, p. 48; April 3, p. 52; April 10, p. 45; April 17, p. 48; April 24, p. 39.)

Continued discussion, by letter, in reply to questions by editor concerning the presence and prevention of corrosion in water-pipe.

**Siebel, E. P.**

Pitting of iron, particularly pipe; its causes and possible preventives. 3,000 w. Ill. 1909. (In *National Engineer*, v. 13, p. 192.)

Paper before the Chicago section of the Society of Brewing Technology.

Regards pitting as due to electrochemical decomposition in the presence of water and dependent upon the homogeneity of the material. Wrought-iron pipe considered more durable than steel pipe.

**Speller, Frank N.**

Wrought pipe-threading and relative durability of steel and iron. 3,000 w. Dr. ill. 1905. (In *Journal of the Canadian Mining Institute*, v. 8, p. 46.)

*The same.* (In *Iron Age*, v. 75, p. 741.)

Review and illustrations of United States Navy Department tests on pitting. Experiments by National Tube Co., showing that, in resistance to corrosion, common iron and Bessemer steel are both slightly superior to charcoal iron.

**Stewart, A. W.**

Corrosion in metal pipes on board ship. 6,200 w. 1903. (In *Transactions of the Institution of Naval Architects*, v. 45, p. 183.)

*The same, abstract.* (In *Engineer*, London, v. 95, p. 374.)

Discussion.

Considers the action of impurities on the pipes, especially of chlorine and organic impurities.

**Thomson, T. N.**

Relative corrosion of wrought iron and soft steel pipes. 2,800 w. Dr. ill. 1908. (In *Heating and Ventilating Magazine*, v. 5, p. 15.)

*The same, slightly condensed.* 2,500 w. (In *Iron Age*, v. 81, p. 434.)

*See also* letter by G. Schuhmann, p. 520.

Paper before the American Society of Heating and Ventilating Engineers.

Conclusion from experiments is that "plain steel pipe is more durable than plain wrought-iron pipe when used to convey hot water and subject only to internal corrosion."

**Wrought-iron pipe versus steel pipe.** 1,300 w. Dr. 1908. (In *Heating and Ventilating Magazine*, v. 5, p. 8)

Contains extracts from a pamphlet published by the Reading Iron Co., claiming that wrought-iron is the more durable.

## BOILERS.

**Baucke, H.**

Beitrag zur metallographie des flusseisens. 1,600 w. Ill. 1899. (In *Baumaterialienkunde*, v. 4, p. 349.)

*The same, in French.* (In Baumaterialienkunde, v. 4, p. 349.)

*The same.* (In Stahl und Eisen, v. 20, pt. 1, p. 260.)

*The same, condensed translation.* 600 w. (In Journal of the Iron and Steel Institute, v. 57, p. 427.)

Microscopic examination of badly corroded boiler tubes.

**Christie, William Wallace.**

Corrosion, 35 p. Ill. 1906. (In his Boiler-waters, p. 68.)

Treats rather fully the corrosion of boilers, the action of different feed-waters and the dangers of pitting.

**Churchill, W. W.**

Preservation of surface condenser tubes in plants using salt or contaminated water circulation. 3,000 w. 1906. (In Science, v. 47, p. 405.)

*The same.* (In Power, v. 26, p. 598.)

Paper before the American Association for the Advancement of Science.

Considers the prevention of electrolytic corrosion. Author presents Oliver J. Lodge's views on electrolytic condition and Faraday's laws of electrolysis as a basis for his views.

**Ford, John D.**

Corrosion of boiler tubes. 5,200 w. Ill. 1904. (In Journal of the American Society of Naval Engineers, v. 16, p. 529.)

*The same, condensed.* 1,000 w. (In Iron and Steel Magazine, v. 10, p. 349.)

Extensive experiments made for the United States Navy Department at the laboratory of the National Tube Co., McKeesport, to determine relative corrodibility of lap-welded Bessemer steel, lap-welded iron, seamless cold-drawn steel and seamless hot-drawn steel boiler tubes.

**Frémont, Ch., & Osmond, F.**

Les sillons de corrosion dans les toles de chaudières à vapeur. 4,200 w. Ill. 1905. (In Revue de métallurgie, v. 2, p. 75.)

Investigation of cause of lines of corrosion in boiler plates.

**Gesellschaft fur Hochdruck-Rohrleitungen.**

Wasserbeschaffenheit und korrosionen. 4,000 w. Ill. 1909. (In its Rohrleitungen, p. 127.)

Considers action of water on iron, especially of boiler-waters, and methods of protection.

**Gibbons, W. H.**

Physical reasons for rapid corrosion of steel boiler-tubes. 800 w. Ill. 1895. (In American Engineer and Railroad Journal, v. 69, p. 157.)

Considers difference in corrodibility of tubes made from the "top" and the "bottom" of an ingot, with its application to the relative corrosion of steel and charcoal iron.

**Kirtley, William.**

On the corrosion of locomotive boilers and the means of prevention. 8,800 w. Ill. 1866. (In Proceedings of the Institution of Mechanical Engineers, v. 17, p. 56.)

Considers corrosion due both to chemical action of water and mechanical action of strain. The trouble may be obviated by removing one of these causes, i. e., by proper boiler design, eliminating springing at joints, etc.

**La Coux, H. de.**

Eaux corrosives et incrusto-corrosives dans les générateurs de vapeur. 14,500 w. 1899. (In Le Génie Civil, v. 36, p. 117, 139, 149.)

Substances causing corrosion and means of prevention.

**McBride, James.**

Corrosion of steam drums. 8,000 w. Ill. 1891, 1894. (In Transactions of the American Society of Mechanical Engineers, v. 12, p. 518; v. 15, p. 1087.)

Includes lengthy discussion.

**Norris, W. J.**

Corrosion in steam boilers. 5,000 w. 1882. (In Transactions of the Institution of Naval Architects, v. 23, p. 151.)

Disagrees with theories of galvanic action; production of hydrochloric acid in boiler by decomposition of water; action of fatty acids produced by decomposition of lubricants, etc. Ascribes all boiler corrosion to simple oxidation by presence in water of free oxygen derived from the air.

**Palmer, J. Edward.**

Corrosion of steel boiler tubes on vessels fitted with turbine engines. 1,000 w. 1907. (In Journal of the American Society of Naval Engineers, v. 19, p. 54.)

*The same.* (In Engineering News, v. 57, p. 426.)

Corrosion caused by copper deposits in the tubes, carried over by the steam from the bronze turbine blades.

**Paul, James Hugh.**

Corrosion in steam boilers. 20 p. Ill. 1891. (In Transactions of the Society of Engineers, v. 31, p. 147.)

Chemical properties of iron; manufacture of boiler plates; corrosive natural waters; artesian well waters; corrosion in marine boilers; action of zinc.

Discussion.

**Rinne, H.**

Kesselmaterial und kesselkorrosionen. 5,000 w. Dr. 1904. (In Stahl und Eisen, v. 24, pt. 1, p. 82.)

Considers the corrosion of boiler tubes of different qualities of iron and the influence of other conditions.

**Worthington, Walter F.**

Corrosion of boiler tubes in the United States Navy. 5,000 w. Pl. 1900. (In *Journal of the American Society of Naval Engineers*, v. 12, p. 589.)

Causes of corrosion are discussed, especially from the action of the different impurities in feed-water.

### STRUCTURAL WORK.

**Kent, William.**

Rapid corrosion of iron in railway bridges. 2,000 w. 1875. (In *Journal of the Franklin Institute*, v. 99, p. 437.)

Considers sulphurous acid one of the most active corrosive agents.

**Marriott, William.**

Strengthening and maintaining of early iron bridges. 10 p. 1905. (In *Minutes of Proceedings of the Institution of Civil Engineers*, v. 162, p. 213.)

Discussion, 47 p.

Maintains that no iron bridge rusts as rapidly as new steel bridges, probably due to want of homogeneity or to segregation in the steel.

**Protecting** low overhead structures from gases and blasts of locomotives. 1,600 w. 1904. (In *Engineering News*, v. 52, p. 371.)

Report of a committee, presenting opinions from many sources.

**Removal** of a steel frame building. 800 w. 1903. (In *Engineering News*, v. 49, p. 113.)

Good condition of steel in Pabst Hotel, New York City, five years after erection.

**Snow, J. P.**

Corrosion of structural steel as affected by its chemical composition. 500 w. 1906. (In *Proceedings of the American Society for Testing Materials*, v. 6, p. 148.)

Suggests investigation of part played by manganese and phosphorus.

### WIRE.

**Cushman, Allerton S.**

Corrosion of fence wire. 31 p. 1905. (In *United States—Department of Agriculture. Farmers' Bulletin*, No. 239.)

*The same, condensed.* 3,000 w. (In *Iron Age*, v. 77, p. 207.)

Investigation undertaken for the mutual advantage of consumer and manufacturer. Claims that the uneven distribution of manganese causes part of the trouble, owing to electrolytic action.

**Rudeloff, M.**

Untersuchungen über die widerstandsfähigkeit von seildrähten gegen rosten. 4,000 w. Ill. 1900. (In Mitteilungen aus den Königlichen Technischen Versuchsanstalten, v. 18, p. 107.)

Results of many tests on the resistance of wire to corrosion. Numerous tables and diagrams.

**CONCRETE REINFORCEMENT.****Breuillé.**

Expériences sur le ciment armé. 4,500 w. Dr. 1902. (In Annales des ponts et chaussées, mémoires, ser. 8, v. 3, 1er trimestre, p. 181.)

*The same, condensed.* 200 w. (In Transactions of the American Society of Civil Engineers, v. 51, p. 124.)

*The same, condensed.* 100 w. (In Taylor & Thompson's Treatise on concrete, plain and reinforced, p. 430.)

Argues against the belief that cement does not attack iron. Chemical union takes place between metal and cement, forming silicate of iron, soluble in water, and unless special care is taken in waterproofing the concrete this salt is dissolved and corrosion takes place.

**Cement** paste for protecting steel. 250 w. 1908. (In Mining and Scientific Press, v. 97, p. 744.)

Successful coating used by the Pennsylvania Railroad, said to be cheap and durable.

**Corrosion** of reinforcing metal in cinder-concrete floors. 2,200 w. 1906. (In Engineering News, v. 56, p. 458.)

Contains report in full of a committee to the Structural Association of San Francisco, recommending that the building laws be so amended as to exclude cinder concrete from use in floor slabs.

*See also* editorial, p. 461.

**Experiment** to indicate whether iron rusts when imbedded in concrete. 150 w. 1904. (In Report of the Boston Transit Commission, v. 10, appendix F, p. 80.)

Two-year tests give excellent results.

**Experiment** to indicate whether steel imperfectly cleaned is preserved from further rusting by imbedding the same in concrete. 200 w. 1904. (In Report of the Boston Transit Commission, v. 10, appendix F 2, p. 81.)

No apparent increase of rust in two years.

**Fox, William H.**

Corrosion of steel in reinforced cinder-concrete. 1,600 w. Dr. 1907. (In Engineering News, v. 57, p. 569.)

Records experiments in which reinforced cinder concrete was exposed to steam and to water for about 40 days. Results showed unmistakable signs of corrosion.

**Himmelwright, A. L. A.**

Corrosion of steel in cinder concrete. 1,200 w. 1907. (In *Iron Age*, v. 79, p. 141.)

Believes that cinder concrete should not be condemned and that the corrosion observed in San Francisco took place during construction.

**Hinrichsen, F. Willy.**

Zur kenntnis des einflusses von koksasche auf den rostangriff von eisen. 1,400 w. 1907. (In *Mitteilungen aus dem Königlichen Materialprüfungsamt*, v. 25, p. 321.)

Found that the sulphur in coke ashes has very little action on iron enclosed in cement and ashes.

**Immunity** from rusting of reinforcing steel in concrete. 900 w. Ill. 1908. (In *Engineering News*, v. 59, p. 524.)

Results of tests at the Prussian Royal Testing Institution, showing that ordinary tension cracks do not allow corroding influences of the atmosphere to affect the steel.

**Knudson, Adolphus A.**

Electrolytic corrosion of iron and steel in concrete. 3,200 w. Diag. dr. ill. 1907. (In *Transactions of the American Institute of Electrical Engineers*, v. 26, p. 1, p. 231.)

Discussion, p. 264. 16,000 w. Diag. dr.

*The same, without discussion.* (In *Electrician*, London, v. 59, p. 213.)

"In no sense can concrete be considered an insulator, and . . . it is from all appearances just as good an electrolyte as any of the soils found in the earth."

**Langsdorf, A. S.**

Electrolysis of reinforced concrete. 1,200 w. Diag. dr. ill. 1909. (In *Journal of the Association of Engineering Societies*, v. 42, p. 69.)

*The same.* (In *Engineering-Contracting*, v. 31, p. 327.)

In general an amplification of earlier experiments of Knudson, confirming his results.

**Lidy.**

Expériences sur l'altération des ciments armés par l'eau de mer. 3,000 w. 1899. (In *Annales des ponts et chaussées, mémoires*, ser. 7, v. 18, 4e trimestre, p. 229.)

Results of experiments indicate that cement is not impermeable to salt water and that in time the action of the water will be destructive.

**Matthews, Ernest R.**

Corrosion of steel reinforcement in concrete. 500

w. 1909. (In Iron and Coal Trades Review, v. 78, p. 544.)

*The same.* (In Mechanical Engineer, v. 3, p. 441.)

Abstract of paper before the Society of Engineers.

Conclusions are that concrete, properly mixed, gives almost perfect protection to steel, with no need for a cement coating.

**Newberry, Spencer B.**

Chemistry of the protection of steel against rust and fire by concrete. 1,700 w. 1902. (In Scientific American Supplement, v. 54, p. 22335.)

*The same.* 1,000 w. (In Engineering News, v. 47, p. 335.)

**Nicholas, U. James.**

Tests on the effect of electric current on concrete. 3,200 w. Ill. 1908. (In Engineering News, v. 60, p. 710.)

Shows that electrolytic corrosion of reinforcing steel takes place at that anode, and that under certain conditions concrete and cement are in no sense insulators.

**Norton, Charles L.**

Corrosion of steel frames of building. 1,500 w. 1902. (In Iron Age, v. 70, Nov. 6, p. 7.)

Report of the Insurance Engineering Experiment Station of the Associated Factory Mutual Fire Insurance Companies, Boston.

Tests to determine the protection afforded to steel by Portland cement concrete. 1,700 w. Ill. 1902. (In Engineering News, v. 48, p. 333.)

Indicate that neat Portland cement is a good preventive of corrosion and that corrosion in cinder concrete is due to rust in the cinders and not to the sulphur.

Corrosion of the steel frames of buildings. 1,800 w. Ill. 1902. (In Technology Quarterly, v. 15, p. 343.)

Tests showing that concrete to be effective in preventing rust must be dense, without voids or cracks, mixed and applied quite fresh to clean metal.

Protection of steel from corrosion. 1,600 w. 1904. (In Engineering News, v. 51, p. 29.)

Laboratory experiments, tending to show that concrete properly applied is an almost perfect preservative.

**Preservation of iron in concrete.** 700 w. 1903. (In Engineering Record, v. 47, p. 554.)

Observations on condition of iron embedded in concrete since 1890.

**Schaub, J. W.**

Some phenomena of the adhesion of steel and concrete. 1,400 w. 1904. (In Engineering News, v. 51, p. 561.)

Points out that a chemical union takes place between the iron and the cement and that this union is dissolved in water.

**Tests** on rusting of steel rods embedded in concrete. 600 w. 1908. (In *Engineering News*, v. 59, p. 525.)

Tests made by J. M. Braxton, United States engineer.

**Thwaite, Benjamin Howard.**

Preservation of iron and steel. 1,900 w. 1906. (In *Iron and Steel Magazine*, v. 11, p. 411.)

From "Concrete and Constructional Engineering."

Calls attention to excellent results obtained by use of cement and concrete coverings.

**Toch, Maximilian.**

Permanent protection of iron and steel. 2,300 w. Ill. 1903. (In *Journal of the American Chemical Society*, v. 25, p. 761.)

Considers that metal work, coated with cement paint, then with hydrocarbon insulating paint, will be perfectly protected when embedded in masonry.

Electrolytic corrosion of structural steel. 1,800 w. 1906. (In *Transactions of the American Electrochemical Society*, v. 9, p. 77.)

*The same, without discussion.* 1,000 w. (In *Chemical Engineer*, v. 4, p. 125.)

*The same, condensed.* 1,500 w. (In *Electrochemical and Metallurgical Industry*, v. 4, p. 215.)

Denies that concrete is a complete protector against corrosion, and cites experiments showing that in structural steel embedded in concrete rapid corrosion takes place at the anode while the cathode is protected.

Electrolytic corrosion of structural steel. 1,300 w. Ill. 1906. (In *Proceedings of the American Society for Testing Materials*, v. 6, p. 150.)

Tests of steel embedded in various mixtures of concrete show that the concrete is no protection unless the steel is otherwise insulated.



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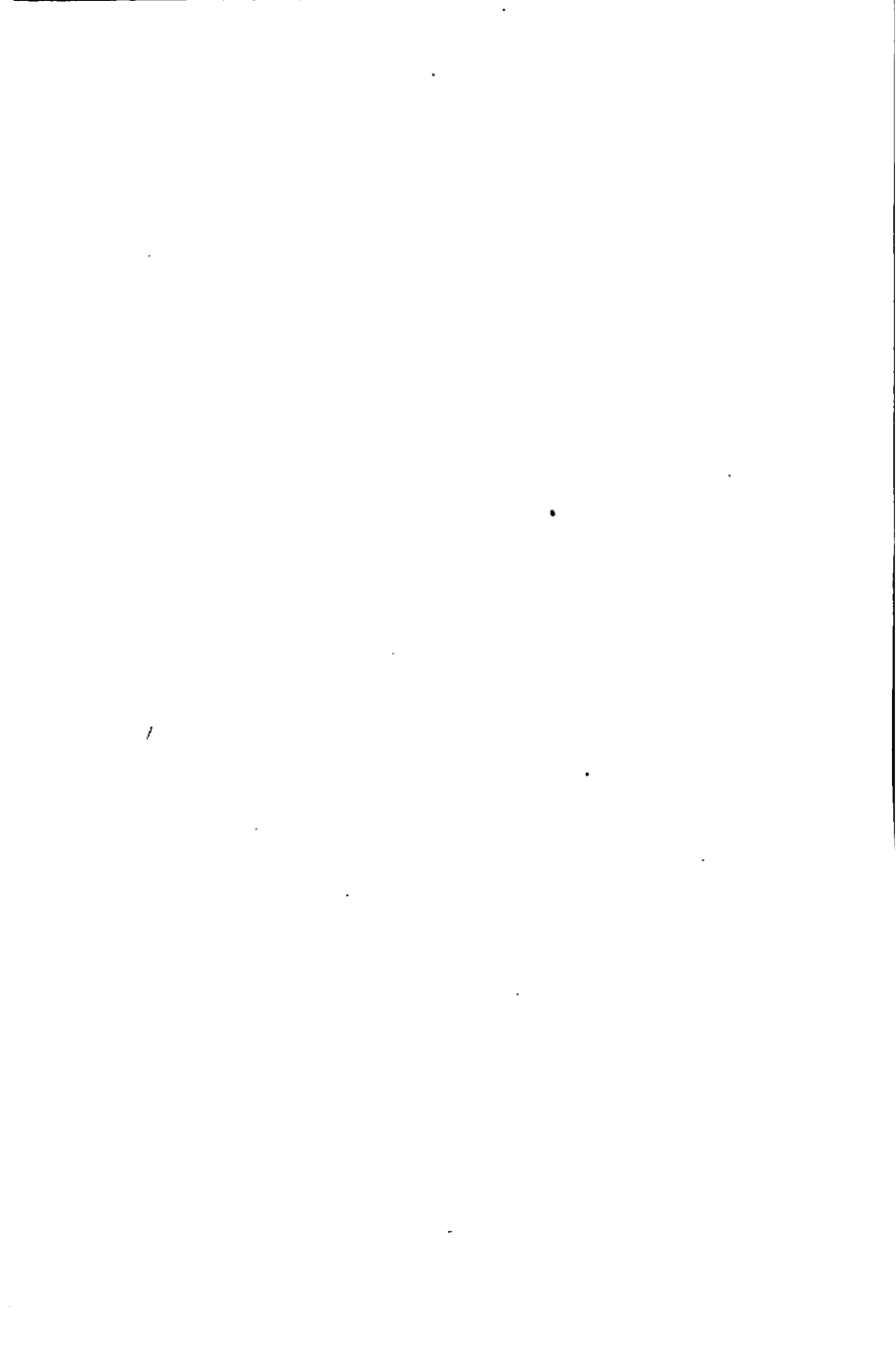
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